

Quantitative Estimation of the Changes in Soil CEC after the Removal of Organic Matter and Iron Oxides

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Abstract

The removal of organic matter and iron oxides could increase and decrease soil CEC in tropical and subtropical regions, but the quantitative information is insufficient so far about the change of soil CEC, the influence factors and their contribution. In this study, the subhorizon soils of 24 soil series in the tropical and subtropical China were used, pH, particle size composition, organic matter, iron oxides of these samples were measured, and also CECs were measured and compared for the original soils and after the removal of organic matter and iron oxides. The results showed that, compared with CEC of the original soil, the eliminating organic matter increased soil CEC significantly by 2.28% - 56.50% with a mean of 24.02%, but the further obliterating iron oxides decreased soil CEC significantly by 0.75% - 20.30% with a mean of 7.73%. CEC after the removal of organic matter and iron oxides had positive correlation with iron oxides ($p < 0.01$) and negative correlation with sand content ($p < 0.01$ and $p < 0.05$). CEC after organic matter eliminated was mainly decided by iron oxides (51.68%), followed by silt content (22.19%); while CEC after iron oxides obliterated was mainly determined by iron oxides (50.55%). The increase of CEC after organic matter eliminated was co-affected by the contents of clays, slits, iron oxides and pH (22.00% - 27.34%), while the decrease of CEC after iron oxides obliterated further was dominated by the content of organic matter (66.92%). More other soil parameters should be considered for higher predicting accuracy in the regression model of soil CEC after the removal of organic matter and iron oxides, and the recommended optimal models obtained in this study were as follows: for soil CEC after organic matter eliminated, $CEC = 1.665 - 0.546pH - 0.024OM + 0.053Fe_xO_y - 0.001Silt + 0.007Clay + 0.972CEC_{original}$ (R^2 was 0.923, RSME was $1.55 \text{ cmol}(+)\cdot\text{kg}^{-1}$, $p < 0.01$), while for soil CEC after iron oxides further

obliterated, $CEC = 1.665 - 0.546pH - 0.024OM + 0.053Fe_xO_y - 0.001Silt + 0.007Clay + 0.972CEC_{original}$ (R^2 was 0.923, RMSE was $1.55 \text{ cmol}(+)\cdot\text{kg}^{-1}$, $p < 0.01$). Further research is needed in the future as for exploring internal functional mechanism in view of soil electrochemistry and mineralogy.

Keywords

Soil CEC, Quantitative Estimation, Removal, Organic Matter, Iron Oxides

1. Introduction

It was found early that CEC of the soils in tropical and subtropical regions would be increased after the removal of organic matter, and then decreased after the further removal of iron oxides [1] [2], the former could be attributed to the adsorption of organic matter by clays [3] [4] [5] [6], which hinders the adsorption of charges, and the latter could be attributed to the characteristics that iron oxides also are partial clays and may dominate soil CEC [7] [8]. However, so far little is known about the change degree of soil CEC after the removal of organic matter and iron oxides, and the influence factors and their contribution. Thus, a brief study was conducted with the typical subhorizon soils from soil series in tropical and subtropical China in order to: 1) disclose the change degree of soil CEC after the removal of organic matter and iron oxides, 2) clarify the influence factors and their contribution to the change degree of soil CEC, 3) establish the predicting model of soil CEC from other parameters after the removal of organic matter and iron oxides.

2. Materials and Methods

2.1. Background of Tested Soil Samples

Figure 1 shows the spatial distribution of 24 soil series used in this study in tropical and subtropical China [9]-[15]. The removal of organic matter and iron oxide were based on the extraction method of soil clays [16] [17], which were mainly as follows: 1) firstly, $0.2 \text{ mol}\cdot\text{L}^{-1}$ and $0.05 \text{ mol}\cdot\text{L}^{-1}$ HCl were used respectively to decompose calcium carbonate and wash away Ca^{2+} from soil samples sieved through 2 mm nylon mesh; 2) secondly, 1:4 H_2O_2 was dropped to the soil samples until no bubbles (CO_2) are presented and the soil color becomes light, indicating organic matter is fully removed; 3) finally, sodium citrate-sodium bicarbonate-sodium disulfite (DCB) was used to dissolve iron oxides in soil samples, and then TG20G high-speed centrifuge was used to fully eliminate away the dissolved iron oxides.

For the determination of soil parameters, the pipette method was used to measure the particle size distribution, the potentiometer method (soil:water = 1:2.5) was used to determine pH value, the Walkley-Black wet oxidation method was used to decide the content of organic matter, the phenanthroline colorimetry

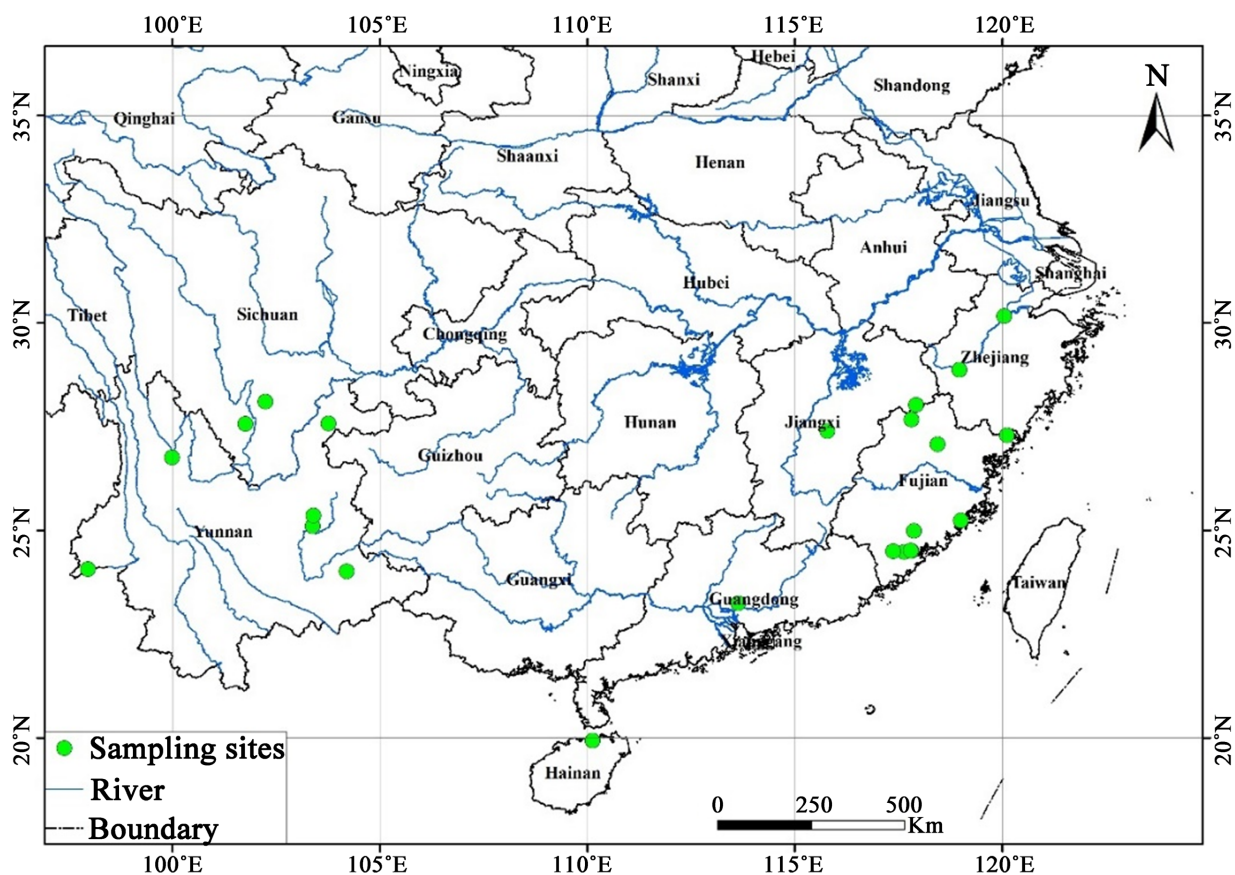


Figure 1. Spatial distribution of 24 soil series used in this study in tropical and subtropical China.

method was used to obtain the content of iron oxides, the NH_4OAc (pH 7.0) exchange method was used to measure the CEC values of original soil sample (CEC_1) and after the removal of organic matter (CEC_2) and iron oxides (CEC_3) [16] [17].

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) were used for variance analyses and multiple comparisons.

3. Results

3.1. Statistical Results of Soil Parameters

Table 1 lists the measured values of soil parameters, it showed that soil CEC was $5.12 - 19.90 \text{ cmol}(+)\cdot\text{kg}^{-1}$ with a mean of $11.16 \text{ cmol}(+)\cdot\text{kg}^{-1}$, after organic matter eliminated, soil CEC significantly increased to $7.36 - 25.71 \text{ cmol}(+)\cdot\text{kg}^{-1}$ with a mean of $13.64 \text{ cmol}(+)\cdot\text{kg}^{-1}$ ($p < 0.01$), increased by 2.28%~56.50% with a mean of 24.02%; but after further iron oxides was obliterated, soil CEC then decreased to $6.97 - 23.68 \text{ cmol}(+)\cdot\text{kg}^{-1}$ with a mean of $12.59 \text{ cmol}(+)\cdot\text{kg}^{-1}$ ($p < 0.01$), decreased by 0.75% - 20.30% with a mean of 7.73%.

3.2. Parameters Influencing Soil CEC

Table 2 lists Pearson correlation between soil CEC with other parameters, it could be found that CEC₁ had positive correlation with iron oxides ($p < 0.01$) and silt content ($p < 0.05$) but negative correlation with sand content ($p < 0.05$). CEC₂ and CEC₃ had positive correlation with iron oxides ($p < 0.01$) but negative correlation with sand content ($p < 0.01$ and $p < 0.05$), while ΔCEC_{3-2} had negative

Table 1. Statal descriptions of soil parameters (n = 24).

Soil parameter	Min.	Max.	Mean \pm S.D.	C.V.(%)	Skewness	Kurtosis
CEC ₁	5.12	19.90	11.16 \pm 4.06	36.36	0.64	-0.75
CEC ₂	7.39	25.71	13.64 \pm 4.80	35.16	0.87	0.13
CEC ₃	6.97	23.68	12.59 \pm 4.58	36.33	1.01	0.13
ΔCEC_{2-1}	2.28	56.50	24.02 \pm 16.62	69.21	0.48	-0.78
ΔCEC_{3-2}	-0.75	-20.30	-7.73 \pm -4.55	-58.89	-0.94	1.40
pH	4.39	6.68	5.17 \pm 0.62	12.07	0.96	0.46
Organic matter	3.10	33.57	10.90 \pm 8.17	74.93	1.39	1.21
Iron oxides	19.25	80.84	41.65 \pm 16.31	39.15	0.71	-0.20
Sand	70	640	302 \pm 168	55.66	0.59	-0.80
Silt	116	517	331 \pm 117	35.18	-0.37	-0.82
Clay	173	596	366 \pm 107	29.27	0.03	-0.09

Note: 1) CEC, $\text{cmol (+)} \cdot \text{kg}^{-1}$; sand, silt, clay, organic matter and iron oxides, $\text{g} \cdot \text{kg}^{-1}$; 2) CEC₁, original soil CEC; CEC₂, soil CEC after organic matter eliminated; CEC₃, soil CEC after organic matter and iron oxides obliterated; $\Delta\text{CEC}_{2-1} = (\text{CEC}_2 - \text{CEC}_1) \times 100/\text{CEC}_1$; $\Delta\text{CEC}_{3-2} = (\text{CEC}_3 - \text{CEC}_2) \times 100/\text{CEC}_2$, The Same Below; 3) data of CEC 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	Organic matter	Iron oxides	Sand	Silt	Clay
CEC ₁	Pearson Correlation	0.116	0.117	0.574**	-0.446*	0.465*	0.193
	Sig. (2-tailed)	0.588	0.586	0.003	0.029	0.022	0.366
CEC ₂	Pearson Correlation	0.030	0.071	0.679**	-0.518**	0.399	0.379
	Sig. (2-tailed)	0.888	0.743	0.000	0.010	0.054	0.068
CEC ₃	Pearson Correlation	0.059	-0.009	0.662**	-0.508*	0.362	0.403
	Sig. (2-tailed)	0.784	0.965	0.000	0.011	0.082	0.051
ΔCEC_{2-1}	Pearson Correlation	-0.243	-0.022	0.241	-0.072	-0.177	0.306
	Sig. (2-tailed)	0.253	0.920	0.256	0.737	0.409	0.147
ΔCEC_{3-2}	Pearson Correlation	0.196	-0.548**	-0.136	0.057	-0.201	0.129
	Sig. (2-tailed)	0.359	0.006	0.526	0.790	0.346	0.548

Note: 1) *, **, Correlation is significant at $p < 0.05$ or 0.01 level (2-tailed).

correlation with organic matter ($p < 0.01$).

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 software to ensure them with the same magnitude, and then the regression coefficients between each parameter with CEC was used to indicate their contribution to CEC [18] [19] [20]. 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 could be roughly seen from **Table 4** that CEC_1 and CEC_2 was mainly decided by the content of iron oxides (47.17% and 51.68%), followed by the content of silts (31.39% and 22.19%); CEC_3 was mainly determined by the content of iron oxides (50.55%); ΔCEC_{2-1} was mainly affected by the contents of clays (27.34%), silts (25.82%), iron oxides (24.73%) and pH (22.00%); ΔCEC_{3-2} was mainly influenced by the content of organic matter (66.92%).

3.3. Correlation between Soil CEC

Table 5 lists Pearson correlation between various soil CEC, positive correlation was found between CEC_1 , CEC_2 and CEC_3 (R^2 was 0.918 - 0.989 with Sig. = 0.000), but no correlation was found between ΔCEC_{2-1} and ΔCEC_{3-2} with CEC_1 , CEC_2 and CEC_3 .

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

Linear regression model	R ²	RMSE	F	Sig.
$CEC_1 = 2.031 \times 10^{-16} - 0.004pH - 0.157OM + 0.550Fe_xO_y + 0.366Silt - 0.089Clay$	0.450	0.84	2.91	0.041*
$CEC_2 = -2.354 \times 10^{-16} - 0.074pH - 0.170OM + 0.631Fe_xO_y + 0.271Silt + 0.075Clay$	0.550	0.75	4.41	0.009**
$CEC_3 = -6.433 \times 10^{-16} - 0.060pH - 0.243OM + 0.640Fe_xO_y + 0.247Silt + 0.076Clay$	0.543	0.76	4.28	0.010*
$\Delta CEC_{2-1} = -6.472 \times 10^{-16} - 0.202pH - 0.001OM + 0.227Fe_xO_y - 0.237Silt + 0.251Clay$	0.223	0.10	1.03	0.429
$\Delta CEC_{3-2} = -4.376 \times 10^{-16} + 0.078pH - 0.532OM + 0.052Fe_xO_y - 0.095Silt - 0.038Clay$	0.314	0.94	1.65	0.199

Note: OM, organic matter; Fe_xO_y , iron oxides.

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

Property	pH	Organic matter	Iron oxides	Sand	Silt	Clay	Total
CEC_1	0.34	13.46	47.17	0	31.39	7.63	100
CEC_2	6.06	13.92	51.68	0	22.19	6.14	100
CEC_3	4.74	19.19	50.55	0	19.51	6.00	100
ΔCEC_{2-1}	22.00	0.11	24.73	0	25.82	27.34	100
ΔCEC_{3-2}	9.81	66.92	6.54	0	11.95	4.78	100

Table 5. Pearson correlation between soil CEC.

CEC	Correlation	CEC ₂	CEC ₃	ΔCEC ₂₋₁	ΔCEC ₃₋₂
CEC ₁	Pearson Correlation	0.927**	0.918**	-0.311	0.057
	Sig. (2-tailed)	0.000	0.000	0.139	0.790
CEC ₂	Pearson Correlation		0.989**	0.051	0.033
	Sig. (2-tailed)		0.000	0.812	0.878
CEC ₃	Pearson Correlation			0.036	0.177
	Sig. (2-tailed)			0.867	0.407
ΔCEC ₂₋₁	Pearson Correlation				-0.130
	Sig. (2-tailed)				0.544

Note: *, **, Correlation is significant at $p < 0.05$ or 0.01 level (2-tailed).

Table 6. Predicting models of clay CEC₇.

	Predicting model	R ²	RMSE	F	Sig.
1	$CEC_1 = 3.453 - 0.024pH - 0.078OM + 0.137Fe_2O_3 + 0.013Silt - 0.003Clay$	0.450	3.60	2.94	0.041
2	$CEC_2 = 5.022 - 0.569pH - 0.100OM + 0.185Fe_2O_3 + 0.011Silt + 0.003Clay$	0.550	3.64	4.41	0.009
3	$CEC_2 = 1.418 + 1.095CEC_1$	0.859	1.84	133.70	0.000
4	$CEC_2 = 1.665 - 0.546pH - 0.024OM + 0.053Fe_2O_3 - 0.001Silt + 0.007Clay + 0.972CEC_1$	0.923	1.55	33.81	0.000
5	$CEC_3 = 4.452 - 0.438pH - 0.136OM + 0.180Fe_2O_3 + 0.010Silt + 0.003Clay$	0.543	3.49	4.27	0.010
6	$CEC_3 = 1.038 + 1.035CEC_1$	0.843	1.85	118.46	0.000
7	$CEC_3 = 1.222 - 0.415pH - 0.063OM + 0.052Fe_2O_3 - 0.002Silt + 0.006Clay + 0.935CEC_1$	0.922	1.49	33.34	0.000

3.4. Predicting CEC₂ and CEC₃ Based on Other Parameters and CEC₁

By using IBM Statistics SPSS, the regression models of CEC₂, CEC₃, ΔCEC₂₋₁ and ΔCEC₃₋₂ with other parameters and CEC₁ were obtained (see **Table 6**), and it could be found by comparison from **Table 6** that Model 3 and Model 4 could be recommended were suitable for the prediction of CEC₂ while Model 6 and Model 7 for the prediction of CEC₃, respectively, in which Model 4 and Model 6 were optimal for CEC₂ and CEC₃ prediction, respectively.

4. Discussions

Our study showed (see **Table 1**) that, for the subhorizon soils in tropical and subtropical China, clay and silt contents were meanly 331 g·kg⁻¹ and 302 g·kg⁻¹ while sand content was only meanly 41 g·kg⁻¹, and iron oxides content was meanly 41.65 g kg⁻¹, which prove further that soils in tropical and subtropical China are clayey and rich in iron oxides [21].

It was found early that CEC of the soils in tropical and subtropical regions would be increased after the removal of organic matter, and then decreased after

the further removal of iron oxides [1] [2]. For the subhorizon soils in tropical and subtropical China, compared with previous studies, our study further quantitatively disclosed the change of soil CEC after the removal of organic matter and iron oxides. The results showed that soil CEC could be significantly increased by 2.28% - 56.50% with a mean of 24.02% ($p < 0.01$) after the elimination of organic matter, and then it could be significantly decreased by 0.75% - 20.30% with a mean of 7.73% after further obliteration of iron oxides ($p < 0.01$). Our study also found that the increased degree of soil CEC after organic matter had no correlation with other parameters (pH, the contents of organic matter, iron oxides and particle size composition (R was 0.022 - 0.306, Sig. was 0.147 - 0.920)); while the decreased degree of soil CEC after iron oxides was obliterated only had negative correlation with the content of organic matter (R was 0.548**, Sig. was 0.1006). In view of the contribution of other parameters to CEC, our study roughly showed that both soil original CEC and CEC after the removal of organic matter were mainly decided by iron oxides (47.17% and 51.68%), followed by the content of silt content (31.39% and 22.19%), but CEC after further obliteration of iron oxides was mainly determined by iron oxides (50.55%); while the increase caused by the removal of organic matter was co-affected by the contents of pH, silts, clays and iron oxides (22.00% - 27.34%), and the decrease resulted from further obliteration of iron oxides was dominantly influenced by OM content (66.92%).

Previous studies showed that pH usually has positive correlation with soil CEC for acid soils [22] [23] [24] [25] [26], however, no significant positive correlation was found in our study between pH and soil CEC (R was 0.116, $p = 0.588$), which could be attributed to narrow range of pH of the soil samples used in our study (acid, 4.39 - 6.68 with a mean of 5.17 in pH). Organic matter usually has significant positive correlation with soil CEC [22] [24]-[34], but our results neither found that organic matter had significant correlation with soil CEC (R was 0.117, $p = 0.586$), which could also be related to the content of organic matter [27] [33] [34] [35] in subhorizon soils used in our study (meanly 10.90 $\text{g}\cdot\text{kg}^{-1}$). Clay content usually also has significant positive correlation with soil CEC [22] [23] [24] [25] [26] [28]-[34] [36], but our results neither found such a phenomenon (R was 0.193, $p = 0.366$), which possibly could be attributed to high content of clay contents in our soil samples (meanly 366 $\text{g}\cdot\text{kg}^{-1}$). Our study found that iron oxides was significantly positively correlated with soil CEC (R was 0.574, $p < 0.01$), few studies analyzed the correlation between iron oxides and soil CEC because iron oxides in subtropical and tropical soils usually exist as clay fraction or strongly cemented with clays [21] [36] [37] [38]. Significant negative correlation was found between soil CEC with sand content in our study, which is consist with the previous studies [22] [31] [33] [34] [35], and could be attributed to sand fraction mainly composed of quartz and iron concretions with low charge density [39]. Moreover, significant positive correlation was also found between soil CEC with silt content in our study as in other studies [23]

[25], which could be attributed to that silt fraction is often composed of vermiculite and mica minerals which can hold negative charges [39] [40].

Removing organic matter and iron oxides from soils and measuring soil CEC are tedious and troublesome processes, so it is helpful to find the predicting model for soil CEC changes after the removal of organic matter and iron oxides if necessary. In our study, various regression models were established, and it was found that model with more parameters usually was higher in accuracy. By comparison, two optimal models are recommended as the optimal predicting model for soil CEC after the removal of organic matter and iron oxides respectively (see **Table 6**, Model 4 and Model 7, with R^2 of 0.923 and 0.922, RMSE of $1.55 \text{ cmol}(+)\cdot\text{kg}^{-1}$ and $1.49 \text{ cmol}(+)\cdot\text{kg}^{-1}$, and $p < 0.01$).

It should be pointed out that our study only focused on quantitative estimating the change degrees of soil CEC after the removal of organic matter and iron oxides and the influence factors and their contribution to the changes, however, further research is needed in the future as for exploring internal functional mechanism in view of soil electrochemistry and mineralogy.

5. Conclusion

Our study quantitatively disclosed the significant increase and decrease of soil CEC after the removal of organic matter and iron oxides in tropical and subtropical China, and found that the increase degree of soil CEC after the elimination of organic matter was co-affected by the contents of clays, slits, iron oxides and pH, while the decrease degree of soil CEC after the further obliteration of iron oxides was dominated by OM content. More other parameters should be considered for higher accuracy in predicting soil CEC after the removal of organic matter and iron oxides.

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Conflicts of Interest

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

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