Surface charge characteristics of a variable charge soil (Rhodic Ferralsols) in the Central Highlands

Quang Chon Nguyen¹*, Van Cuong Dinh¹, Minh Ngoc Truong²

¹Institute of Agricultural Sciences for Southern Vietnam
²Branch of National Center for Technological Progress in Ho Chi Minh city

Received 25 February 2020; accepted 4 May 2020

Abstract:
Variable charge soils (VCS) predominantly contain minerals with variable surface charge density, such as kaolinite, gibbsite, goethite, hematite and amorphous minerals. The charge characteristics differ between profile horizons, the topsoil normally possesses net negative surface charge whereas the subsoil may have net positive surface charge and are largely dependent on soil pH. The soils pose a particular challenge to sustainable management in terms of low cation exchange capacity (CEC) at soil low pH and may develop appreciable anion exchange capacity (AEC) under acidic conditions. A full understanding of the variation of charge with soil pH, before establishing strategies for sustainable management of these soils, is essential. This study has found that the VCS from the Central Highlands are extremely acidic (pH<4.5) and very low in CEC (<1.0 cmol$_{c}$ kg$^{-1}$), these problems are more pronounced in the subsoil with exhibiting higher pH$_{0}$ (4.63) than the existing soil pH (4.26) and higher point of zero net charge (PZNC) (4.88) than point of zero charge (pH$_{0}$), and developing net positive surface charge (-0.62 cmol$_{c}$ kg$^{-1}$). These properties are attributed to low total organic carbon (TOC) and Fe/Al hydrous oxides in the clay fraction that significantly affect pH buffering capacity and delta CEC. In addition, organic matter (OM) has a great influence on the pH$_{0}$ of variable charge components, and thus on CEC.

Keywords: cation exchange capacity, point of zero charge, surface charge, variable charge soil.

Classification number: 3.1

Introduction

VCS are the soils that have developed under intensive weathering and leaching conditions in tropical and subtropical regions that contain minerals with variable surface charge density, such as kaolinite, gibbsite, goethite, hematite, and amorphous minerals [1, 2]. The charge characteristics of VCS can differ between profile horizons, even within a single soil type. In general, it is found that the surface charge of the topsoil possesses a net negative charge whereas the subsoil may have a net positive surface charge, which is so-called the ‘geric property’ [3].

Point of zero charge (PZC), or pH$_{0}$, is the pH value at which the variable net surface charge, resulting from the adsorption of potential determining ions H$^{+}$ and OH$^{-}$, is zero. This value is of fundamental significance to the characterization of VCS [4]. For instance, if the soil pH is below pH$_{0}$, the variable charge sites will carry net positive charge. In contrast, if a soil pH is above pH$_{0}$, they will carry a net negative charge. Because the charge characteristics of VCS are largely dependent on soil pH, soil acidification often has severe consequences on the fertility of these soils. For example, the decrease in CEC, as a consequence of acidification, results in lower retention capacity for base cations which leads to the possibility of Al and/or Mn toxicities. Thus, it is essential to identify a soil’s sensitivity to pH changes to establish appropriate soil pH management schemes.

Although VCS in its natural state maintain highly productive and diverse ecosystems, they pose a particular challenge to sustainable management in terms of low values of CEC at soil pH and rapid reduction in CEC, particularly base CEC$_{up}$, as soil acidity increases [5]. On the other hand, these soils (particularly in the subsoil or B horizon) develop appreciable AEC under acidic conditions and can retain leachable anions such as nitrate and sulphate [2]. Due to these intrinsic characteristics, surface charge properties are of central importance to the management of VCS. Therefore, it is essential to determine the in situ CEC and obtain a full
understanding of the variation of charge with pH before establishing strategies for sustainable management of these soils.

Materials and methods

Soil collection and preparation

Red soil derived from basalt rock (Rhodic Ferralsols, according to FAO/UNESCO soil classification) under maize cultivation was collected from the Chu Pah district, Gia Lai province, Vietnam, and used in this study. Two soil samples were taken from depths between 0-20 and 20-40 cm. Each soil sample at a particular depth was collected from three similar maize-cultivated fields with five different subsamples per field and was well mixed. The soil samples were air-dried and passed through a 2 mm-sieve before determining their charge characteristics and analysing the physicochemical properties of the soils. The study was conducted in the laboratory of the Institute of Agricultural Sciences of Southern Vietnam from March to August 2018. The clay contents and selected chemical characteristics of the soil are given in Table 1.

Table 1. Clay contents and selected chemical characteristics of the studied soil.

<table>
<thead>
<tr>
<th>Depths (cm)</th>
<th>Clay (%)</th>
<th>(%) TOC</th>
<th>(%) Al(_{ox})</th>
<th>(%) Fe(_{ox})</th>
<th>(%) Si(_{ox})</th>
<th>(%) Al(_{cryst})</th>
<th>(%) Fe(_{cryst})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-20</td>
<td>62</td>
<td>2.50</td>
<td>0.30</td>
<td>0.28</td>
<td>0.01</td>
<td>1.8</td>
<td>14.1</td>
</tr>
<tr>
<td>20-40</td>
<td>65</td>
<td>1.55</td>
<td>0.38</td>
<td>0.34</td>
<td>0.01</td>
<td>2.6</td>
<td>16.6</td>
</tr>
</tbody>
</table>

\(\%\) TOC, \(\%\) oxalate extractable Al; \(\%\) oxalate extractable Fe; \(\%\) oxalate extractable Si; \(\%\) crystalline Al; and \(\%\) crystalline Fe.

Analytical determinations

The following methodologies were used to determine the properties of the soils: particle size analysis on dispersed samples as described by [6]; TOC by the 6B2B method [7]; oxalate extractable Fe, Al and Si (Fe\(_{ox}\), Al\(_{ox}\), and Si\(_{ox}\), respectively) by the 13A1 method [7]; and citrate bicarbonate dithionite Fe and Al (Fe\(_{cbo}\) and Al\(_{cbo}\), respectively) by the 13C1 method [7].

Charge fingerprints, which are the curves describing the charge characteristics of soil such as the total CECT, CECB, and AEC, were determined using methodology described by Gillman (2007) [8]. The charge characteristics of the soils were ascertained at a solution ionic strength (IS) similar to field conditions (IS=0.006; this is considered to be the typical IS of weathered tropical soils). As shown in Fig. 1, the pH values of the six suspensions of each soil sample were adjusted over the pH range of 4.0 to 7.0, i.e. 4.0, 4.6, 5.2, 5.8, 6.4, and 7.0, using 0.1 M HCl and 0.02 M Ca(OH)\(_2\). The charge fingerprints can also determine the soil pH, the pH buffering capacity (pHBC), the point of zero charge (pH\(_0\)), and the PZNC [8].

Fig. 1. The charge fingerprints of the charge characteristics, consisting of the total cation exchange capacity (CEC\(_T\)), the base cation exchange capacity (CEC\(_B\)) and anion exchange capacity (AEC).

Data analysis

Charge fingerprint curves were plotted using Microsoft Office Excel. Charge characteristic values were calculated using the regression equations derived from the charge fingerprint curves. The general analysis of variance (ANOVA) and standard error of means were used to compare differences between the means of the charge fingerprint curves of the soil layers. Linear correlation coefficient (r) matrices were also computed for the various analyses of the soils to express the relationships of surface charge characteristics with soil properties. All analyses were undertaken by GenStat Discovery Edition 3 (7th edition).

Results

The average pH of the soil was very low, being pH 4.40 and 4.26 in the topsoil (0-20 cm) and subsoil (20-40 cm), respectively (Table 2). The buffering capacity was high in the topsoil, 5.81 cmol\(_{c}\) kg\(^{-1}\) pH unit\(^{-1}\), and reduced to 4.21 cmol\(_{c}\) kg\(^{-1}\) pH unit\(^{-1}\) in the subsoil. The pH\(_0\) and PZNC in the top layer of the soil were not captured by the titration curve (Fig. 2A) or the net charge curve (Fig. 3A) within the pH range of 4.0 to 7.0. Therefore, the pH\(_0\) value of the topsoil (3.81), shown in Table 1, was estimated by extrapolation of the regression equation of the curve (Fig. 2A). The pH\(_0\) in the subsoil was 4.63 and markedly higher than that in the topsoil (3.81). This value was also higher than the existing soil pH (4.26) at this depth. In addition, the PZNC was identified in this layer as 4.88 which is higher than the pH\(_0\) (Table 2).
Table 2. Means and standard error of means (in brackets) for soil pH, pH<sub>0</sub>, PZNC, and pHBC of the soil at different soil depths.

<table>
<thead>
<tr>
<th>Soil depth (cm)</th>
<th>Soil pH (1:5)</th>
<th>pH&lt;sub&gt;0&lt;/sub&gt;</th>
<th>PZNC</th>
<th>pHBC (cmol&lt;sub&gt;c&lt;/sub&gt; kg&lt;sup&gt;-1&lt;/sup&gt; pH unit&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-20</td>
<td>4.40 (±0.18)</td>
<td>3.81 (±0.07)</td>
<td>n.e.</td>
<td>5.81 (±0.27)</td>
</tr>
<tr>
<td>20-40</td>
<td>4.26 (±0.21)</td>
<td>4.63 (±0.05)</td>
<td>4.88</td>
<td>4.21 (±0.19)</td>
</tr>
</tbody>
</table>

<sup>1</sup>Not estimated; ± values are standard errors of the average calculated from six subsamples within the pH range of 4.0 to 7.0.

Table 3. Means and standard error of means (in brackets) for CEC<sub>B</sub>, CEC<sub>T</sub>, and AEC at soil pH of the soil at different soil depths.

<table>
<thead>
<tr>
<th>Soil depth (cm)</th>
<th>CEC&lt;sub&gt;B&lt;/sub&gt; (cmol&lt;sub&gt;c&lt;/sub&gt; kg&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>CEC&lt;sub&gt;T&lt;/sub&gt; (cmol&lt;sub&gt;c&lt;/sub&gt; kg&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>AEC (cmol&lt;sub&gt;c&lt;/sub&gt; kg&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-20</td>
<td>0.49 (±0.03)</td>
<td>0.54 (±0.03)</td>
<td>-0.08 (±0.02)</td>
</tr>
<tr>
<td>20-40</td>
<td>0.23 (±0.01)</td>
<td>0.24 (±0.01)</td>
<td>-0.62 (±0.05)</td>
</tr>
</tbody>
</table>

Both CEC<sub>B</sub> and CEC<sub>T</sub> were extremely low at the pH of the existing soil; approximately 0.50 cmol<sub>c</sub> kg<sup>-1</sup> for the topsoil and 0.25 cmol<sub>c</sub> kg<sup>-1</sup> for the subsoil (Table 3). Over the entire pH range, the CEC<sub>B</sub> and CEC<sub>T</sub> were nearly identical, particularly in the case of the subsoil (Fig. 2B). The soil had positive charges (AEC) in both layers (Table 3). At soil pH, the AEC is -0.62 cmol<sub>c</sub> kg<sup>-1</sup> in the subsoil, which was higher than that of the topsoil (-0.08 cmol<sub>c</sub> kg<sup>-1</sup>). Surface charge characteristics of the soil are presented in Table 4. The total net charge had a very low value of <0.5 cmol<sub>c</sub> kg<sup>-1</sup> in the topsoil. Although a net negative charge was found in the topsoil, the subsoil exhibited a net positive charge, i.e., a net AEC. The soil is dominated by variable charge surfaces in both soil layers, with variable charge accounting for more than 50% of the total net charge (Table 4).
Table 4. Means and standard error of means (in brackets) for total net charge, net permanent and net variable charge of the soil at different soil depths.

<table>
<thead>
<tr>
<th>Soil depth (cm)</th>
<th>Total net charge (cmol, kg⁻¹)</th>
<th>Net permanent charge (cmol, kg⁻¹)</th>
<th>Net variable charge (cmol, kg⁻¹)</th>
<th>Percentage of variable charge (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-20</td>
<td>0.46 (±0.02)</td>
<td>0.20 (±0.09)</td>
<td>0.26 (±0.11)</td>
<td>56.5</td>
</tr>
<tr>
<td>20-40</td>
<td>-0.39 (±0.05)</td>
<td>-0.18 (±0.03)</td>
<td>-0.21 (±0.02)</td>
<td>53.8</td>
</tr>
</tbody>
</table>

Discussion

Variations in soil pH and pH buffering capacity

Soil pH is the most important factor influencing the surface charge of VCS. The quantity of variable charge on a surface is determined by both the dissociation of H⁺ ions from the surfaces and the adsorption of H⁺ ions by the hydroxylated surface as a function of pH of the medium. Therefore, in order to determine the surface charge of a given soil; the existing pH of that soil should be taken into account.

The average pH of the soil in this study ranged from 4.26 to 4.40, classifying the soil as very acidic, which is within the typical pH range of highly weathered soils in tropical regions [9, 10]. Perhaps because of the lower pHBC of the subsoil relative to the surface layers, we find the pH value of the subsoil to be lower than that of the topsoil (Table 2). One reason for this is the response of the subsoil to a given proton sink from weathering processes and land use [11, 12].

Many researchers have found that OM and clay content are the two most important factors influencing pHBC [1, 13, 14]. Buffering capacity is also associated with oxide content [1] and the amount of variable charge [1, 5, 15]. All these authors indicated that pHBC increased with increasing content of OM, clay, and sesquioxide, and with greater amounts of variable charge. Our pHBC results are interpreted in the light of these findings. Table 5 indicates that pHBC is highly correlated (p<0.01) with TOC and FeOx. The pHBC values of the soil decreased with increasing soil depth (Table 2) and this is attributed to the smaller amounts of TOC contained in the subsoil (Table 1). Additionally, in studies on 40 acidic surface soils from Queensland, Aitken, et al. (1990) [16] found that the buffering capacity was significantly (p<0.001) correlated with TOC and clay content (R²=0.88), with TOC being the most important factor. Thus, from the results of the present study, it can be concluded that OM is an important factor responsible for pHBC.

Table 5. Linear correlation coefficient (r) for the relationships between selected soil properties and pH buffering capacity and surface charge characteristics.

<table>
<thead>
<tr>
<th>¹TOC</th>
<th>Clay</th>
<th>²AlOx</th>
<th>³FeOx</th>
<th>⁴SiOx</th>
<th>⁵AlCryst.</th>
<th>⁶FeCryst.</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH₉</td>
<td>0.09</td>
<td>0.81</td>
<td>0.32</td>
<td>-0.03</td>
<td>-0.30</td>
<td>0.54</td>
</tr>
<tr>
<td>ΔCEC</td>
<td>0.69</td>
<td>0.09</td>
<td>0.73</td>
<td>0.84</td>
<td>-0.20</td>
<td>0.11</td>
</tr>
<tr>
<td>pHBC</td>
<td>0.96</td>
<td>0.23</td>
<td>0.75</td>
<td>0.95</td>
<td>-0.62</td>
<td>0.57</td>
</tr>
</tbody>
</table>

*: p<0.05; **: p<0.01; ***: p<0.001; ¹Total organic carbon; ²Oxalate extractable Al; ³Oxalate extractable Fe; ⁴Oxalate extractable Si; ⁵Crystalline Al, and ⁶Crystalline Fe.

Variations in surface charge characteristics

The pH₀ of VCS is considered to be of essential significance because its position relative to the existing soil pH determines the CEC and AEC of the soil. In addition, pH₀ can be used to estimate the net permanent charge of a soil if it is located within the pH range of the charge fingerprint curves [8, 17].

Generally, pH₀ decreases with increasing OM and increasing amounts of minerals having substantial isomorphous substitution (i.e. negatively charged materials). pH₀ also tends to increase with increasing amounts of Fe and Al hydrous oxides [18] as these materials carry some positive charge at low pH [19]. In the present study, the subsoil was very low in TOC content (1.55%) and very high in Fe hydrous oxides (16.6%) (Table 1). Consequently, the subsoil exhibited a high value for pH₀ (4.63) and it was higher than the soil pH (4.26) (Table 2), leading to the net positive charge surface at soil pH as indicated by high AEC (-0.62 cmol, kg⁻¹) and very low CEC (0.23 cmol, kg⁻¹) (Table 3). This result is consistent with the work of Gillman (1985) [4] for oxidic soils from north Queensland and Anda, et al. (2008) [10] for Malaysian Oxisols, which suggested that OM together with iron oxides influenced pH₀ by masking mineral surfaces. All these authors concluded that pH₀ was reduced by about one unit for each one percent increase in organic carbon. These results are also strongly supported by the finding of Gillman (1984) [20] on another VCS from the wet tropical coast of north Queensland under sugarcane cultivation. This author found that the increase in pH₀ values with soil depth reflected the rapid decrease in OM and dominance of oxidic minerals such as goethite and hematite in the clay fraction.

The greater amount of AEC in the subsoil reflects the influence of Fe and Al hydrous oxides, which are positively charged below their points of zero charge [5]. Thus, even though soil pH values did not alter appreciably with soil
These properties are attributed to TOC and Fe/Al hydrous oxide in the clay fraction, which significantly affect pHBC and delta CEC. In addition, OM has a great influence on the pH₀ of variable charge components, and thus on CEC. Consequently, OM addition to the soil will be an important management strategy to improve soil fertility.

The authors declare that there is no conflict of interest regarding the publication of this article.

REFERENCES


Conclusions

Variable charge soil (Rhodic Ferralsols) from the Central Highlands poses several constraints to crop production, such as extreme acidity and very low CEC, and these problems are more pronounced in the subsoil. In particular, the subsoil exhibits higher pH₀ than the existing soil pH and higher PZN than pH₀. Therefore, the soil has developed a net positive surface charge due to its AEC exceeding its CEC. These properties are attributed to TOC and Fe/Al hydrous oxides in the clay fraction, which significantly affect pHBC and delta CEC. In addition, OM has a great influence on the pH₀ of variable charge components, and thus on CEC. Consequently, OM addition to the soil will be an important management strategy to improve soil fertility.


