Threshold electrolyte concentration for dispersive soils in relation to CROSS

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Most investigations of clay dispersion have concentrated on soils with high exchangeable sodium. Traditional indices for assessing soil structural stability, sodium adsorption ratio (SAR) and exchangeable sodium percentages (ESP) do not take into account the effects of K on soil clay dispersion and swelling. Therefore, a new quantitative index, cation ratio of structural stability (CROSS), was used as an alternative to SAR, to take into account the differential effects of Ca, Mg, Na and K on soil structural stability as well as exchangeable cation ratio percentage (ERC) instead of ESP to take into account the effect of exchangeable potassium. In this study we investigated the relationships between threshold electrolyte concentration (TEC) of soil solutions to CROSS for three soils of different mineralogy (illite-kaolinite and smectite), soil texture, net charge, pH and EC. The TEC, when all soils are included correlates with CROSS with $R^2=0.93$. These relationships are different according to individual type of soil. The significant relationships between CROSS of the soil solution and exchangeable cation ratio (ECR), as well as CROSS and turbidity were established for all three soils when data combined together as well as for every individual soil.

Key words: clay dispersion, soil structure, flocculating power, dispersive potential.

Introduction

Sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP) are currently used as indices for assessing the soil structural stability on interaction with water. A few studies have shown that potassium and magnesium ions in the exchange complex of soil can also be related to clay dispersion even when the exchangeable sodium levels are minimal (Arienzo, Christen et al. 2009; Rengasamy 2006; Robbins 1984; Smiles 2006; Subba Rao and Rao 1996). Rengasamy and Marchuk (2011) proposed a new ratio ‘CROSS’ (cation ratio of soil structural stability) analogous to SAR but which incorporates the differential effects of Na and K in dispersing soil clays, and also the differential effects of Mg and Ca in flocculating soil clays, and is defined as: CROSS = $(Na + 0.56K) / [(Ca + 0.6Mg)/2]^{0.5}$ where the concentrations of these ions are expressed in millimole of charge/L. In studies conducted since the introduction of this concept, CROSS has been shown to be superior to SAR in predicting hydraulic conductivity changes and clay dispersion in a number of soils (Jayawardane, Christen et al. 2011; Laurenson, Bolan et al. 2012; Rengasamy and Marchuk 2011). We (Rengasamy and Marchuk, 2011) also found that CROSS measured in soil solutions was strongly correlated with to the ratio of exchangeable cations (ECR %). The primary aim of this paper is to establish threshold electrolyte concentration for a dispersive soil in relation to CROSS of the soil solution.

Methods

Three soils viz. Urrbrae, McLaren and Claremont were used in the present study. Soil samples were air-dried and sieved to 2 mm particle diameter. Selection of these soils was based on the differences in their texture, clay mineralogy, electrical conductivity and pH (Table1). The soils were pre-treated using two sets of treatment solutions, with total cation concentrations 20 and 40 meq/L respectively of CROSStr values of 6, 8, 11 and 15, with gradual increase in concentrations of cations, particularly K. Soil samples were packed into Plexiglas columns at a bulk density of 1.3 Mg/m$^3$. The columns were percolated with three wetting, draining and drying cycles using each of eight CROSS treatment solutions (CROSStr) for Urrbrae and McLaren soils, and seven for Claremont soil. At the end of the last cycle the deionised water was passed through the columns to simulate the infiltration of the soils with rain water. The experiments were conducted using duplicate samples. The soils were removed from the columns, air dried, crushed and passed through a 2-mm sieve.

Spontaneous dispersion and turbidity measurements

Spontaneous dispersion was assessed by a modification of the method described by Rengasamy (2002). Samples (10g) of dry soils were placed into transparent cylinders and 50 ml of distilled water was added slowly down the sides of the cylinders, taking care to avoid disturbance of the soil. After approximately 5 hr, any particles which had dispersed from the soils were gently stirred into suspension and left to stand
for 2 hours. Suspensions were pipetted out from 10 cm depth for turbidity measurements. To quantify the amount of < 2µm particles dispersed, measurements were made on a Hach 2100N Laboratory Turbidimeter at 25°C and recorded in Nephelometric Turbidity Units (NTU).

**Table 1 Selected soil properties**

<table>
<thead>
<tr>
<th>Soil properties</th>
<th>Units</th>
<th>Soil</th>
<th>Units</th>
<th>Soil</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth</td>
<td>cm</td>
<td>Urrbrae</td>
<td>15-40</td>
<td>McLaren</td>
<td>15-40</td>
</tr>
<tr>
<td>pH (1:5 soil water solution)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.7</td>
<td>7.3</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>EC (1:5 soil water solution)</td>
<td>dS/m</td>
<td>0.061</td>
<td>0.139</td>
<td>1.03</td>
<td></td>
</tr>
<tr>
<td>Total carbon</td>
<td>%</td>
<td>1.49</td>
<td>0.76</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>CEC&lt;sub&gt;eff&lt;/sub&gt;</td>
<td>cmol kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>8</td>
<td>10</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>Dominant clay minerals</td>
<td></td>
<td>Illite-kaolinite</td>
<td>Illite-kaolinite</td>
<td>Smectite</td>
<td></td>
</tr>
<tr>
<td>Australian Classification (Isbell 2002)</td>
<td></td>
<td>Red Chromosol</td>
<td>Red-Brown Earth</td>
<td>Vertisol</td>
<td></td>
</tr>
<tr>
<td>Texture</td>
<td></td>
<td>Sandy loam</td>
<td>Clay-loam</td>
<td>Clay</td>
<td></td>
</tr>
<tr>
<td>Location in South Australia</td>
<td></td>
<td>Waite Research Institute</td>
<td>McLaren Vale</td>
<td>Waite Research Institute</td>
<td></td>
</tr>
</tbody>
</table>

The EC and pH of the equilibrium solution were measured and the suspensions were then centrifuged. Soluble cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) (concentrations mmolc/L) were determined in the 1:5 extracts by ICP. CROSSs of the soil solutions were calculated using the following equations:

\[
\text{CROSSs} = \frac{(\text{Na} + 0.56\text{K})}{[\text{(Ca} + 0.6\text{Mg})/2]^{0.5}} \text{ (mol0.5m-1.5)} \quad (1)
\]

where the concentrations of the corresponding ions are expressed in mmolc/L.

The exchangeable cations (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) were determined by the method described in Rayment and Lyons (2011) and subsequently exchangeable cation ratio percentage (ECR %) were calculated as:

\[
\text{ECR %} = \left[ \left( \text{Na}^++\text{K}^+ \right) / \text{CEC}_{\text{eff}} \right] \times 100\% \quad (2)
\]

where the quantities of the exchangeable cations are expressed in cmole/kg.

**Results**

Clay dispersion in relation to CROSS

Chorom and Rengasamy (1995) concluded that clay dispersion was highly related to the net particle charge influenced by mineralogy and pH as well as organic carbon. Therefore, it cannot be expected that a relationship between the amount of clay dispersion and CROSS would be similar for the different types of soils. Nevertheless, for the three treated soils used in this study, the clay dispersion measured by the turbidity was highly correlated with CROSSss, with R<sup>2</sup> = 0.88 (Fig.1). As for an individual soil type, although the slopes of the regressions differed significantly, correlations for all three soils were high:

- Urrbrae soil: \(Y=1746.2X-3776\) R<sup>2</sup>=0.89
- McLaren soil: \(Y=1889.6X-3199\) R<sup>2</sup>=0.78
- Claremont soil: \(Y=1633X-2975\) R<sup>2</sup>=0.76.

**Figure 1. Relationships between CROSSss and turbidity for all soils.**
Smectitic Claremont soil had clay dispersion even at low CROSSss values and the turbidity was lower than the illitic soils, confirming our earlier results (Rengasamy and Marchuk, 2011)

Threshold electrolyte concentration in relation to CROSSss
Cationic effects on soil structural features such as clay dispersion are highly influenced by the corresponding electrolyte concentration which promotes flocculation. For a given value of CROSSss, the electrolyte concentration needed to completely flocculate the clay suspension (or, in other words, completely prevent dispersion) is termed as 'threshold electrolyte concentration (TEC)' (Rengasamy 2002). Similar to the earlier derivations of TEC relating SAR or ESP for different soils (e.g. Quirk and Schofield, 1955; Rengasamy et al. 1984) we have obtained the relation between CROSSss and TEC (Fig 2) at the point of complete flocculation as follows: \( Y = 0.45 \times X + 0.5 \), where \( Y \) is TEC (dS/m) of the flocculated suspensions and \( X \) is CROSSss of the dispersed soil suspensions.

![Graph showing relationships between threshold electrolyte concentration (TEC) and cation ratio of structural stability of soil solutions (CROSSss) for all soils.](image)

Both CROSSss and ECR% of the dispersed soil solutions were highly correlated with the experimentally estimated TEC in individual soil types (Table 2). Similar quantitative relationships for different soil types are necessary for proper soil management. Once developed, these equations will be the basis for maintaining soil structure by adding or maintaining electrolytes below the concentration of which soil physical problems affect soil drainage and indirectly affect plant growth.

<table>
<thead>
<tr>
<th>Soil</th>
<th>X</th>
<th>Y</th>
<th>Regression equation</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urrbrae</td>
<td>CROSS</td>
<td>TEC</td>
<td>( Y = 0.36X + 0.91 )</td>
<td>0.96</td>
</tr>
<tr>
<td>McLaren</td>
<td></td>
<td></td>
<td>( Y = 0.35X - 1.17 )</td>
<td>0.97</td>
</tr>
<tr>
<td>Claremont</td>
<td></td>
<td></td>
<td>( Y = 0.31X + 0.58 )</td>
<td>0.94</td>
</tr>
<tr>
<td>Urrbrae</td>
<td>ECR%</td>
<td>TEC</td>
<td>( Y = 0.09X - 2.35 )</td>
<td>0.75</td>
</tr>
<tr>
<td>McLaren</td>
<td></td>
<td></td>
<td>( Y = 0.085X - 0.9 )</td>
<td>0.89</td>
</tr>
<tr>
<td>Claremont</td>
<td></td>
<td></td>
<td>( Y = 0.017X + 0.58 )</td>
<td>0.89</td>
</tr>
</tbody>
</table>

*Statistical calculations and linear regression analysis were performed with the programme Graphpad Prism version 5.01 (GraphPad Software, Inc., San Diego, USA).
Conclusion
We studied dispersive soils using the newly developed concept of cation ratio of structural stability (CROSS). We investigated the relationships between threshold electrolyte concentration (TEC) of soil solutions to CROSS for three soils of different mineralogy (illite-kaolinite and smectite), soil texture, total carbon, pH and EC. Across all soils, the TEC highly correlated with CROSS ($R^2=0.93$). However, the relationships are different for individual soils. Illitic soils differ from smectitic soils, particularly in the slope values. Significant relationships between CROSS of the soil solution and exchangeable cation ratio (ECR), were established for all three soils as well as for each individual soil. Different cations with their specific flocculating power are involved in TEC. Future research will concentrate on using TEC for estimation of the amount of inorganic electrolytes needed to prevent clay dispersion by introducing the flocculating power of the individual cations in the flocculating suspension.

References