Cation ratio of soil structural stability (CROSS)

Alla G Marchuk and Pichu Rengasamy

Soils group, School of Agriculture, Food and Wine Prescott building, Waite Campus, The University of Adelaide, Adelaide, 5005 S.A. Email alla.marchuk@adelaide.edu.au

Abstract

Sodium salts tend to dominate salt-affected soils and groundwater in Australia and therefore, sodium adsorption ratio (SAR) is being used to parameterize soil sodicity and the effects of sodium on soil structure. Recent reports, however, now draw attention to elevated concentrations of potassium and/or magnesium in some soils naturally and also as a result of increasing irrigation with recycled water in Australia. Therefore, there is a need to derive and define a new ratio of these cations in place of SAR, which will indicate the effects of Na and K on clay dispersion and Ca and Mg on flocculation. Rengasamy and Sumner (1998) derived the flocculation power of these cations and on this basis Rengasamy (unpublished) defined the cation ratio of soil structural stability (CROSS). This paper gives the results of an experiment conducted on ten soil samples on hydraulic conductivity using a number of artificially prepared irrigation waters, containing different proportions of the cations Ca, Mg, K and Na. The relative changes in hydraulic conductivity of these soils reflected the flocculating power of the cations, compared to the control treatment of using $CaCl_2$ solution. Clay dispersion was found to be highly correlated to CROSS rather than to SAR.

Key Words

Sodicity, soil structure, irrigation, potassium, cations

Introduction

About 35% of total land area in Australia is affected by different categories of salt-affected soils. Apart from natural salinity, significant proportion of the cultivated land has become saline due to irrigation, particularly when groundwater or recycled waste waters were used. Sodium salts tend to dominate salt-affected soils and groundwater in Australia. When sodium ions are adsorbed by soil particles as exchangeable cations, soil becomes sodic and the soil structure is degraded by means of clay swelling and dispersion. Exchangeable potassium can also cause similar effects, but has been neglected because of low amounts present in salt-affected soils. Some studies (Emerson and Bakker 1973) have implicated the role of magnesium ions in enhancing the clay dispersion in some sodic soils.

Traditionally, exchangeable sodium percentage (ESP) is used as a measure of soil sodicity and is related to soil structural degradation through clay dispersion from soil aggregates. Critical values of ESP to define soil sodicity differs in different parts of the world because several factors including electrolyte concentration, pH, organic matter content and clay mineralogy affect the ESP value above which clay dispersion or reduction in soil hydraulic conductivity occurs. Measurement of ESP is time consuming and therefore, sodium adsorption ratio (SAR) measured in soil solution which is highly correlated with soil ESP is conveniently used as a measure of soil sodicity and, in part, the effects of sodium on soil structure.

Recent reports, however, now draw attention to elevated concentrations of potassium and/or magnesium in some soils naturally and also as a result of increasing irrigation with waste or effluent or recycled water in Australia. There is also a tendency in industries to use potassium or magnesium salts instead of sodium during process to prevent the increase in sodium concentration in effluents. Smiles (2006) reported that there is, on average, more water-soluble and exchangeable potassium than sodium across a range of soils in the Murray-Darling Basin. He concluded that neglect of potassium and simple appeal to SAR to infer soil structural stability will be misleading. Many sodic soils, particularly subsoils, in Australia have higher exchangeable magnesium than calcium. Rengasamy *et al*. (1986) concluded that the enhanced clay dispersion in high magnesic sodic soils is due to the lower flocculating effect of Mg compared to Ca.

Concept development

Sodium adsorption ratio is defined as follows:

$$SAR = Na/[(Ca + Mg)/2]^{1/2}$$

where concentrations of Na, Ca and Mg are expressed as mill moles of charge/L. Potassium, being a monovalent cation, can cause clay swelling and dispersion. But, potassium appears not equivalent to sodium in causing structural problems in soils (Rengasamy and Sumner 1998) although early basic colloid studies showed an almost exact correspondence between the effect of sodium and potassium in 'simple' aqueous suspensions of lyophobic colloids (Hunter 1993).

A Monovalent Cations Adsorption Ratio (MCAR), defined by

$$MCAR = (Na+K)/ [(Ca + Mg)/2]^{1/2}$$

has been suggested by Smiles and Smith (2004) to meet this need. This ratio may predict the adsorption of monovalent ions by soil colloids on the basis of cation exchange isotherms, but it fails to weight the relative efficacies of Na and K in the numerator and of Ca and Mg in the denominator and treats members of each pair as identical.

Therefore, there is a need to derive and define a new ratio of these cations in place of SAR, which will indicate the effects of Na, K, Mg and Ca on soil structural stability. This will be achieved using a formula analogous to the SAR but which selectively incorporates the dispersive effects of Na and K on the one hand with the flocculating effects of Ca and Mg on the other. Rengasamy and Sumner (1998) derived the flocculating power of these cations on the basis of Misono softness parameter responsible for hydration reactions and the ionic valence. They defined the flocculating power as:

$$\text{Flocculating power} = 100(I_z / I_{z+1})^2 Z^3$$

where I_z and I_{z+1} are zth and z+1 ionisation potential of a cation with valence Z. Thus, the relative flocculating powers of cations are: Na=1, K=1.8, Mg=27 and Ca=45 (see Rengasamy (2002) for details). Flocculating power gives the reverse of dispersive effects. Based on these notions a ratio analogous to the MCAR but which incorporates the differential effects of Na and K in dispersing soil clays, and the differential effects of Ca and Mg in flocculating soil clays, may be written:

$$\text{Cations Ratio of Structural Stability (CROSS)} = (Na+0.56K)/[(Ca +0.6\ Mg)/2]^{1/2}$$

Where the concentrations of these ions (Na, K, Ca and Mg) are expressed in milli moles of charge/L (Rengasamy, unpublished). The total concentration of the cations, together with this formula should, more generally and effectively, parameterize soil structural effects of the relative amounts of monovalent and divalent cation in the soil solution than any previous approach. The development is critically important in view of current concerns about salinity definition and management in Australia.

Experimental Results

Saturated hydraulic conductivity of a clay loam soil was determined after saturating with solutions: a) pure $CaCl_2$ (0.005 M) b) SAR 10 with Na and Ca c) SAR 10 with Na and Mg d) PAR (potassium adsorption ratio) 10 with K and Ca and e) PAR 10 with K and Mg, using appropriate solutions of chlorides of Na, K, Mg and Ca. The EC of the percolating solutions were about 0.5 dS/m. The following Table shows the differential effects of Na, K, Mg and Ca on the hydraulic conductivity which is a measure of soil structural stability.

Table 1. Effect of SAR or PAR 10 solutions with either Ca or Mg as accompanying cation on soil saturated hydraulic conductivity.

Salts used	Cations	SAR or PAR	Saturated hydraulic conductivity (mm/day)
$CaCl_2$	Ca only	-	100
NaCl and $CaCl_2$	Na/Ca	10	19.8
NaCl and $MgCl_2$	Na/Mg	10	12.4
KCl and $CaCl_2$	K/Ca	10	40.6
KCl and $MgCl_2$	K/Mg	10	26.9

Ten sodic soils from different locations in South Australia were collected on the basis of different concentrations of exchangeable potassium, magnesium and calcium in addition to sodium. SAR of the soil solutions (1:5 soil-water extract) and % of clay spontaneously dispersed clay were determined by the method described by Rengasamy (2002). CROSS was also calculated using the equation given above from the concentrations of Na, K, Mg and Ca in the same soil solutions. The correlation between SAR and % dispersed clay and the correlation between CROSS and % dispersed clay are given in the following figures:

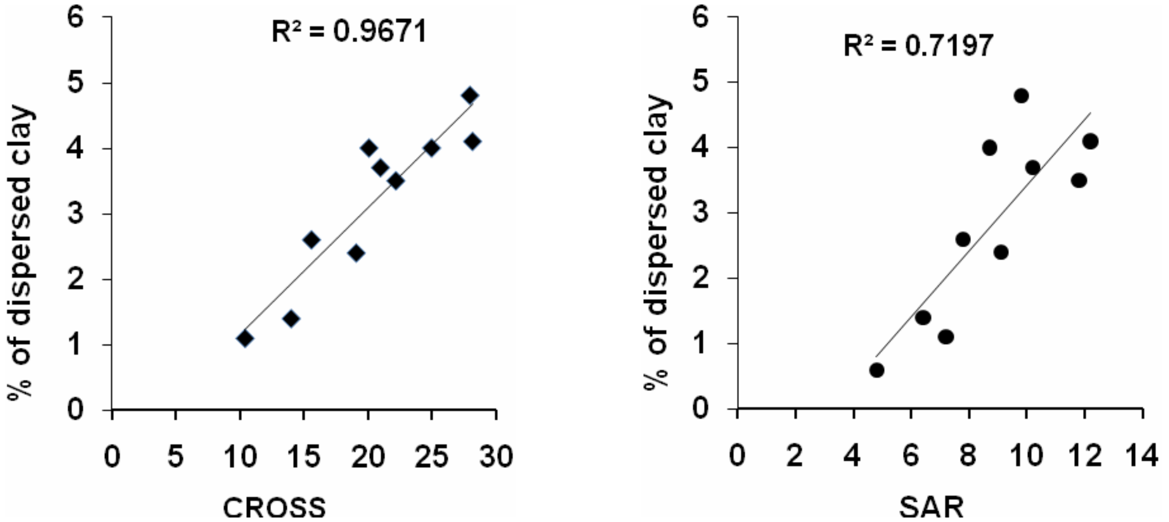

Figure 1. Relationships between CROSS, SAR and percentage of dispersed clay.

The results indicate that the correlation between CROSS and % dispersed clay is highly significant with an $R^2 = 0.9671$, a high improvement from the R^2 value for the correlation between SAR and % dispersed clay which was only 0.7197.

Further studies in progress

CROSS is a new concept and its validity is not yet tested. To validate and make use as a parameter in soils and irrigation water, our experiments are in progress to investigate the following:
Applicability of CROSS as an index of structural stability over a range of soils containing varying quantities of Na, K, Mg and Ca and also anions such as chloride, sulphate and carbonate. Similar to the utility of SAR, the effects of CROSS on structural stability will depend largely on the total electrolyte concentration and soil texture. The influence of mineralogy, organic matter and pH are also important. Researching the various factors influencing the efficacy of CROSS, we hope to derive useful threshold values.

References

Emerson WW, Bakker AC (1973) The comparative effects of exchangeable calcium, magnesium, and sodium on some physical properties of red-brown earth subsoils. II. The spontaneous dispersion of aggregates in water. *Australian Journal of Soil Research* **11**, 151-157.

Hunter RJ (1993) Introduction to Modern Colloid Science Oxford University Press, Oxford, New York.

Rengasamy P (2002) Clay dispersion, pp. 200-210, *In* 'Soil Physical Measurement and Interpretation for Land Evaluation' (McKenzie BM *et al* Eds.). CSIRO Publishing, Collingwood.

Rengasamy P, Sumner ME (1998) Processes involved in sodic behaviour, *In* 'Sodic Soils. Distribution, Properties, Management, and Environmental Consequences' (Sumner ME, Naidu R, Eds.), pp. 35-50. New York Press, New York.

Rengasamy P, Greene RSB, Ford GW (1986) Influence of magnesium on aggregate stability in sodic red-brown earths. *Australian Journal of Soil Research* **24**, 229-237.

Smiles D, Smith C (2004) A survey of the cation content of piggery effluents and some consequences of their use to irrigate soil. *Australian Journal of Soil Research* 42, 231-246.

Smiles DE (2006) Sodium and potassium in soils of the Murray-Darling Basin: a note. *Australian Journal of Soil Research* **44**, 727-730.