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Peer-reviewed version available at *Agronomy* **2018**, *8*, 72; doi:10.3390/agronomy8050072

Review

Irrigation water quality and soil structural stability: a perspective with some new insights

Pichu Rengasamy

School of Agriculture, Food and Wine, Prescott Building, Waite Campus, The University of Adelaide,
Adelaide, 5005 SA, Australia; pichu.rengasamy@adelaide.edu.au; Tel.: +61-8-8313 7418

Abstract: The sustainability of irrigated agriculture depends on the quality of irrigation water used. The electrolyte concentration (EC) of irrigation water may lead to the accumulation of salts in the root zone layers and affect the physiological functions of the crop by osmotic and ion toxicity effects. Further, the cationic and anionic composition of the water may alter the exchangeable cation composition of the soil and as well as its pH. Because of the dominance of sodium salts in many sources of irrigation water, parameters related to sodium such as exchangeable sodium percentage (ESP) of soils and sodium adsorption ratio (SAR) of soil solutions have been commonly used to study the effects of sodium in irrigation water on soil structural stability. Quirk and Schofield concept of 'threshold electrolyte concentration' (TEC) has shown the importance of electrolytes in preventing the effects of sodium on soil structure. Based on this concept, several models have been proposed to relate ESP or SAR with EC to predict the possible impacts of irrigation water on soil structural stability. However, many research reports indicate that this relationship varies with soils and a given model is not suitable for all types of soils. Further, the effects of potassium and magnesium in the processes leading to clay dispersion are disregarded in these models. This essay analyses all the factors involved in the structural failure of soils with different cationic composition, identify the defects in these TEC models and re-defines TEC on the basis of new insights on dispersive and flocculating charges of soils. This review does not deal with EC effects on crops and also the role of contaminant ions not involved with soil structural stability.

Keywords: Water quality; Soil Structure; Threshold electrolyte concentration; Zero point of dispersion

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1. Introduction

Irrigation of soils is an important component of productive agriculture particularly in regions where rainfall is not sufficient to provide enough water to be used by crops during their growth and yield cycles. Because of increase in yield potential and economic benefits, areas of irrigated agriculture are increasing since the beginning of agricultural civilization in ancient times. However, productivity of irrigated agriculture is low in many parts of the world because of the poor quality of irrigation water impacting on soils and crops. Good quality water with low amounts of dissolved salts has been found to be always beneficial when used in productive soils. But, with increasing salt concentration in the water, decreasing crop growth and yield have been observed. In hostile soils, other soil constraints can also add to the stress on crops.

Salinity of irrigation water may lead to the accumulation of salts in soil layers above a threshold level and impact on crops by osmotic and ion toxicity effects [1]. While the total concentration of salts in irrigated soils relates to the osmotic effects, the ionic composition determines ion toxicity and/or plant nutritional disorders. Further, cationic and anionic composition of irrigation water alters the adsorbed ionic status of the charged sites on soil components and also pH of soil water. Sodium dominant saline water from sources such as groundwater or waste water is commonly used when supplies of good quality water are limited or non-existent. This leads to high levels of adsorbed

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sodium in soils and deterioration of soil structure, with reduced infiltration and water movement, poor soil tilth, inadequate aeration, waterlogging and anoxic conditions [2,3].

As the level of soil sodicity, commonly estimated as exchangeable sodium percentage (ESP), increases, soil aggregate stability in water declines because of increased swelling and dispersion of clay particles. But, these effects of increasing ESP are altered by the presence of electrolytes in soil water. Quirk and Schofield 1955, in their widely cited 'Landmark Paper' [4,5], proposed the concept of 'threshold electrolyte concentration' (TEC), which is the electrolyte concentration (EC) in soil water above which the physical properties of a soil at a given ESP are not affected by sodicity. Based on this principle, several models have been proposed[e.g. 6,7,8,9,10,11,12 among others] relating ESP and EC of soils to either clay dispersivity or changes in hydraulic conductivity, and identifying TEC to maintain soil structural stability. In many instances, sodium adsorption ratio (SAR) of irrigation water or soil solution is used instead of ESP to determine sodicity. The observations by these researchers have clearly shown that TEC varies widely in relation to many soil factors, and is a unique value for a given soil. However, soil managers and environmental consultants still choose and follow one of these models, and decide the quality of water (based on SAR and EC values), and its suitability for irrigation to all the soils they are dealing with, irrespective of varying soil factors.

The aims of this essay are: 1. Outline the basics of soil structural stability in water and analyse the various soil factors involved in swelling and dispersive behaviour of soils in relation to cationic and anionic composition of soil water. 2. Identify the deficits in the models based on threshold electrolyte concentration concept. 3. Propose possible modification of the TEC concept based on new insights. 4. Articulate conclusions and suggest future studies needed. This essay does not deal with irrigation water quality in relation to 'salinity' effects on crops, although the author recognizes its importance in management decisions related to improved productivity of irrigated crops. Also, the role of toxic contaminants, not involved in soil structural processes, is not discussed.

1. Soil structural stability in water

(i) Aggregation of soil particles and water stability of aggregates

Soil structure refers to the heterogeneous arrangement of soil particles bound together as aggregates of different sizes and the resultant formation of different sized pores and their continuity, enabling soil physical processes such as movement of water and air. Soil structural stability is the ability of these aggregates to retain this arrangement when exposed to various externally applied stresses[13]. Different sized aggregates form by the combination of clay, silt, sand and other inorganic and organic materials linked by several bonding mechanisms. These aggregates within soil clods have been classified in a hierarchical order, mainly on the basis of their size, ranging from clay floccules, domains, clusters, micro aggregates, macro aggregates through to clods, although not all of these hierarchical orders exist in all soils[14]. Breakdown of larger aggregates into smaller ones occurs as a result of externally applied mechanical stress such as by tillage implements, when the applied energy exceeds the bonding strength of the particle linkage. But, on wetting, the strength of aggregates are weakened significantly leading to their breakdown, irrespective of the force of application of water.

On wetting 'slaking' of soil clods can occur where macro aggregates are disintegrated into micro aggregates. This phenomenon does not always destroy soil structure but introduces different soil structural forms which may not necessarily affect soil physical conditions conducive for crop production. However, the swelling and eventual dispersion of clay particles from aggregates by the interaction of water molecules with clay surfaces destroys all the hierarchical orders and the soil structure is degraded significantly affecting soil physical properties, as experienced in sodic soils [14]. Swelling and dispersive behaviour of sodic soils originate from the interaction of polar water molecules with electrical fields induced by positive and negative charges on soil particles, particularly soil colloids. While in polar solvents, the degree of slaking and dispersion depends on the dielectric constant of the solvent and ESP of soil aggregates, in relatively nonpolar solvents with very low dielectric constants, slaking and dispersion of soil aggregates do not occur irrespective of

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their sodicity levels (Table 1). Similarly, aggregates of particles without any net surface charge (available for hydration reactions) do not slake or disperse in water. Chorom and Rengasamy1996 showed that a Na-smectite when heated above 300^{0}C, did not swell or disperse due to the absence of hydration charge as a result of the covalent bonding of Na with clay structure [15].

Table 1. Slaking and dispersion of Alfisol aggregates (2-4 mm) at two levels of sodicity in various solvents [16].

Solvent	Dielectric constant at 25^{0}C	Slaking % <2mm ESP 1	Slaking % <2mm ESP 20	Dispersed clay as % of total clay ESP 1	Dispersed clay as % of total clay ESP 20
Water	78.5	67	80	0	26
Ethanol	24.3	24	12	0	6
Benzene	2.3	0	0	0	0
n-Hexane	1.9	0	0	0	0

(ii) Processes leading to structural changes on wetting of dry aggregates

The mechanisms proposed by soil scientists for clay swelling and dispersion based on the double layer DLVO theory [17] are mainly applicable to colloids in aqueous suspensions. This theory has been found unsatisfactory in clays with divalent cations, where diffuse double layer formation is restricted to stacking or aggregation of particles [18,19]. Further, it does not account for the forces due to different cations involved as counter ions, and also the crystalline swelling of divalent ion saturated clays in high electrolyte concentrations [20]. In dry soils, clays are confined within aggregates and not suspended in water. To understand the mechanisms of slaking and dispersion of soil aggregates, it is necessary to take into account all the processes that occur during initial wetting of dry aggregates which result in swelling in the first stage to the final stage of aggregate disintegration, leading to dispersion of soil clays when completely wet. The magnitude and direction of energy changes due to hydration of charged sites during wetting of an aggregate are illustrated schematically in Figure 1 and the following discussions are based on the report by Rengasamy and Sumner 1998 and Rengasamy *et al*. 2016[16,21].

The energy involved in hydration reactions depends on the electrical charge available in soil particles. The net electrical charge depends on the type and amount of clay minerals, organic matter and other inorganic constituents. Although the net charge can be calculated on the basis of the charge on the individual components, the charge available for hydration is altered because of the different types of bonding among these components [22]. For example, soil clays are complex intergrowths of different clay structures intimately associated with inorganic and organic molecules and biopolymers; as a result, they do not have same charge characteristics as the pure clay mineral counterparts of the soil clay mineral identified by x-ray diffraction methods. The layer charge of clay minerals contributed by isomorphous substitution may be large, but the charge available for hydration may be quite different as observed in illites where K is bound to layer charge by inner-sphere complexation and smectites with charge originating from tetrahedral substitution leading to inner-sphere complexation of cations, including Na [23,24]. Inner-sphere complexation of cation or molecule involves covalent bonding by clays resulting in hydrophobicity, whereas outer-sphere complexation of cation involves ionic bonding (electrostatic attraction) facilitating hydration.

When a dry aggregate is wetted (stage 1; Figure 1), the initial attractive force between particles decreases significantly due to the repulsive hydration forces and the pressure in the

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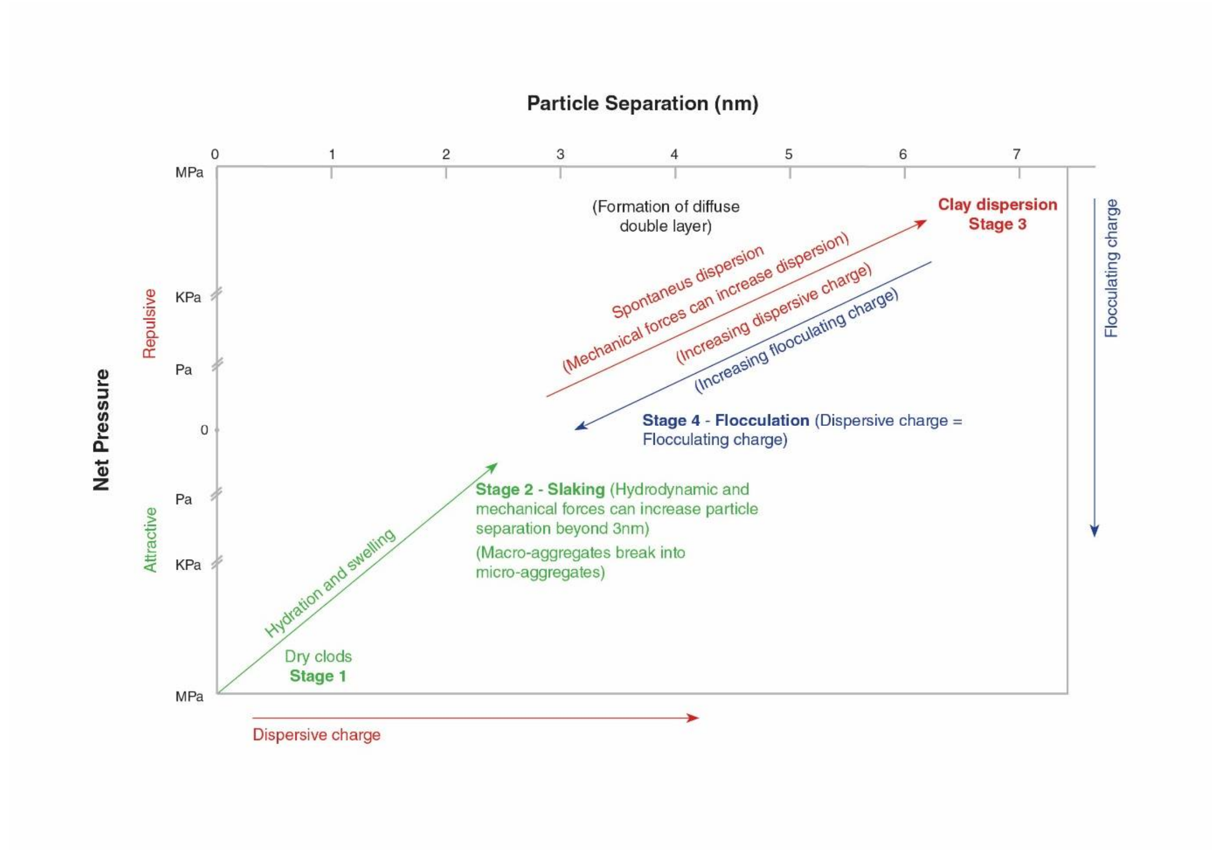

Figure 1. Particle separation from soil aggregates on wetting due to net pressure generated by dispersive and flocculating charges.

Mega Pascal (MPa) range. As the water content increases and hydration continues, the distance between the particles increases to 2-3 nm, which is the stage of swelling (Figure 1) and the aggregate strength is reduced from MPa range to kPa or Pa range. Although very weak, the net force is still attractive and the particles are held by hydrated cations. If these cations are divalent, further hydration is restricted because of low ionicity of clay-cation bonding [25]; and the particles are not separated beyond 2-3 nm. Mg-clays swell more than Ca-clays [26,27] , presumably because of higher ionicity of Mg bonds than Ca bonds. This ‘crystalline swelling’ of divalent cationic clays can occur even when soil water is highly saline; macroscopic swelling being higher in low electrolyte concentrations [23]. Even though the particles are attracted with the net pressure in the kilo Pascal range, hydrostatic and pneumatic pressures in the range of kilo Pascal associated with pore filling are sufficient to break the weak linkage between particles and the linked units become separated via a process which is known as ‘aggregate slaking’ (stage 2; Figure 1). The hypothesis that the mechanical stress due to the displacement of entrapped air during wetting or raindrop impact is the major reason for slaking is untenable. Unless the particle linkages are weakened by electrostatic interactions by polar water molecules, the low pressures associated with entrapped air or raindrop impact will fail to cause disintegration of aggregates, as observed in aggregates treated with non-polar solvents [16,28].

As water content increases, extensive hydration of clays dominant in monovalent cations such as Na and K occurs. These monovalent cations which are bonded to clays with higher ionicity compared to Ca and Mg, and this leads to particle separation beyond 7 nm. At this stage of clay dispersion (Stage 3, Figure 1) the particles are completely separated from each other without any attraction to each other (i.e. not aggregated). This process known as ‘spontaneous dispersion’ occurs because of macroscopic swelling with repulsive pressures of kilo Pascal magnitude.

The clay particles saturated by divalent ions (Ca and Mg) which have been separated up to 2-3 nm by swelling pressures, can be pushed further apart by applying external mechanical pressure in

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the range of Pascal to kilo Pascal such as occurs with shaking or raindrop impact. When they are separated beyond 7 nm, the clay particles are dispersed with no attraction to each other and this process is known as 'mechanical dispersion'. Ca or Mg clay aggregates can be dispersed when uniformly remoulded (i.e. with energy input) at or above critical water content, defined by Emerson 1983 [29] as water content for dispersion. At lower water contents, attractive forces dominate in spite of the mechanical repulsive pressure introduced by remoulding. Dispersion will be enhanced by remoulding or mechanically shaking when the inorganic cements, such as calcium carbonate, surrounding the aggregate are broken. Similarly mechanically broken bonds between clay and organic matter can act as peptizing agents, enhancing the ease of dispersion of soil [30]. In the field, tillage can cause this external mechanical pressure [8].

Dispersed clay particles come closer together when the difference in the chemical potential of water in inner and outer solutions approaches zero. As an example, when the pH of the clay suspension reaches the value of point of zero charge (PZC), the clays flocculate [31].When soil water contains dissolved electrolytes, the electrostatic repulsive pressure is balanced by the increasing flocculating pressure at which stage the components of attractive pressures such as Lifshitz-van der Waals forces become active. At this stage flocculation or coagulation (used synonymously in soil science) occurs in clay or soil suspensions with high water content (Stage 4, Figure 1) and the 'flocculation value' in the suspension is termed the 'threshold electrolyte concentration'. On drying, the flocculated clay particles are increasingly attracted to each other; attractive pressures are far greater and depend on the bonding type of the cations. This association is termed as aggregation, or 'flocculation plus'. When soil water content is below saturation (or field capacity) and the electrolyte concentration is equal to or above flocculation value, limited swelling of aggregate can occur. Extensive swelling and further dispersion on increasing the water content are prevented by the flocculating pressures (or flocculation powers) of the dissolved cations.

(iii) Repulsive forces in relation to cations and anions

The net electrical charge on soil particles is contributed by the type of associated clay minerals, inorganic materials and organic matter. These charges are reduced when the components of an aggregate are linked by covalent bonding. According to thermodynamic principles, these charges have to be balanced by oppositely charged elements or molecules in order to be in a stable equilibrium. Generally, most of agricultural soils (except perhaps Ferrosols, equivalent of Oxisols) have net negative charge, and the charges are balanced by exchangeable cations, most commonly by Na, K, Mg and Ca. Exchangeable Al, Fe and Mn can also be involved in acidic soils. While Na, K, Mg, Ca ions are hydrated (or solvated) by water molecules, Al, Fe and Mn hydrolyze water molecules and form different positively charged hydroxy cations [32,33] which are usually bound to clays by covalent bonding. In soils with net positive charge (as in Oxisols), the charge is balanced by exchangeable anions, such as chloride, sulphate and phosphate.

The bonds between exchangeable cations and clay particles (also clay-organic complexes) were thought to be completely ionic. However, recent advances in inorganic chemistry have shown that any given heteronuclear bond found in natural systems has a mixture of covalent and ionic character. Covalent bonding between a cation and an anion is favoured on the basis of their polarizability. Thus, the resultant ionicity or covalence of a cation bond with an anion will also be influenced by the nature of the anion. For example, the ionicity of Ca^{2+} in $CaCl_2$ is higher than in $CaCO_3$. This is also reflected in their water solubility; $CaCl_2$ being highly soluble compared to the very low solubility of $CaCO_3$.

Marchuk and Rengasamy 2011 [25] hypothesized that, because of both increasing charge and increasing size of a clay particle, the electron cloud in the bond formation will be less influenced by the clay anion, and thus the covalency or ionicity index of a cation alone will indicate the ionic character of a clay-cation bond. These authors derived the covalency index (CI) of a clay-cation bond which is defined by:

$$CI = (I_z / I_{z+1})\, Z^{0.5} \qquad (1)$$

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where Z is the valence of the cation whose ionization potential is I_z, and I_{z+1} is the ionization potential when the valence of the cation changes to Z+1. Values of CI are ≤1.

The ionicity index (II) is then defined as II = 1-CI. The ionicity index of a clay-cation bond indicates the reactivity of water molecules disrupting the bond. Marchuk and Rengasamy 2011 [25] reported that the clay behaviour in aqueous suspensions such as turbidity (i.e. clay dispersion), zeta potential or mean particle size of different homoionic soil clays e.g. Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+} or Ba^{2+} ,was highly correlated to their respective ionicity indices. Ionicity of clay-cation bonds determines the dispersive power of the adsorbed cations. It can be concluded that the inherent hydration charge of a soil is a result of the unique combination of its mineral and organic components as well as pH, and is balanced by exchangeable cations, which is then altered by the degree of ionicity of clay-cation bonds.

(iv) Net dispersive charge in relation to clay dispersion

The degree of ionicity of clay-cation bonding indicates water interaction, but swelling and dispersion depend on the dispersive power of cations [21]. These authors defined the 'dispersive charge' of a soil as:

$$\text{Dispersive charge} = (\text{Ca}) + 1.7\ (\text{Mg}) + 25\ (\text{K}) + 45\ (\text{Na}) \qquad (2)$$

Where concentrations of exchangeable cations measured at the given soil pH are expressed as cmol_c $\text{kg}^{-1}$and the coefficients of each cation are their respective dispersive powers relative to Ca, and derived from the ionicity of clay-cation bonds.

The dispersive charge is reduced by the flocculating effects of cations present in electrolytes in soil solutions. Rengasamy *et al*. 2016 [21] also defined the 'flocculating charge' as follows in Equation 3:

$$\text{Flocculating charge} = 45(\text{Ca}) + 27\ (\text{Mg}) + 1.8\ (\text{K}) + (\text{Na}) \qquad (3)$$

Where the concentration of soluble cations in the dispersed (or flocculated) soil-water suspension is expressed as cmol_c kg^{-1}(on soil basis). The weighting factors of the cations are based on the flocculating powers of cations as discussed in [16], and are inversely proportional to the coefficients of the dispersive powers.

In dispersed suspensions, the 'net dispersive charge' (Dispersive charge – Flocculating charge) determines the amount of clay dispersed [21]. The Zeta potential of the dispersed clay is highly correlated with the net dispersive charge [34,35] indicating the importance of electrostatic forces involved in clay dispersion and flocculation processes [36]. At zero point of dispersion (the point of complete flocculation), dispersive charge equals flocculating charge. Hence, threshold electrolyte concentration can be redefined as the flocculating charge at the point of zero dispersion.

2. Deficits in the models based on Quirk-Schofield concept on 'Threshold electrolyte concentration'

In their Landmark paper [4], Quirk and Schofield 1955 defined the threshold concentration of the electrolyte as the concentration that led to a 10-15% decrease of sodic soil permeability from its initial value measured at non-sodic conditions. In the absence of electrolytes, sodicity reduced the permeability to a great extent. This concept led to the practical application of electrolytes such as gypsum to combat the sodicity effects on soil physical conditions, and also to distinguish sodic (dispersive) soils from saline (flocculated) soils (Figure 2, where sodic soils are referred as dispersive soils). The models published on the basis of this concept used ESP or SAR as parameters of sodicity and EC (either as electrical conductivity or total cation concentration) for electrolyte concentration. Relating these two parameters to changes in hydraulic conductivity, TEC was derived as the point where the level of reduction in hydraulic conductivity was permissible for good plant functions. Some used clay dispersion-flocculation processes instead of changes in soil permeability [e.g. 8].

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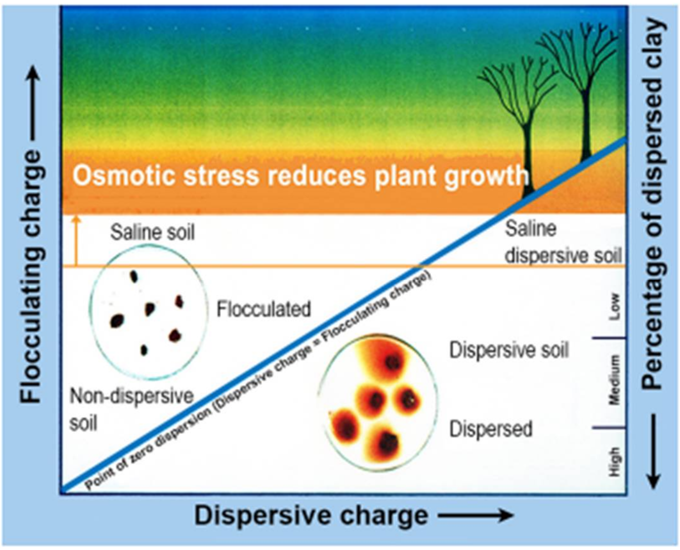

Figure 2. Distinction between saline and sodic (dispersive) soils based on dispersive charge, flocculating charge and percentage of dispersed clay. (After Rengasamy 2016 [37], with permission from MDPI CC BY 4.0). Point of zero dispersion represents TEC.

It is now widely known that TEC- SAR (or ESP) relationship is not universal, but unique for each soil. Several publications have revealed that many soil factors such as organic matter, clay content and mineralogy, cementing agents and soil pH affect swelling, dispersion and flocculation besides sodicity and salinity [22, 38, 39, 40]. For example, Blackmore 1976 [41] and McIntyre 1979 [42] have shown that 'subplastic' soils in Australia with an ESP of 25-30 do not disperse and the hydraulic conductivity of these soils was independent of ESP. Because of cementation by several compounds including sesquioxides and carbonates, probably reducing the dispersive charge, these soils are not sensitive to increasing ESP. So and Aylmore 1993 [43] and Sumner 1993 [44] conclude that no simple definition of sodic soil based on a single ESP value is possible. Table 2 presents these soil factors and the mechanisms involved in controlling soil dispersive behaviour. Bennett and Raine 2012 [45], after experimenting with several soils, concluded that there are significant differences between TEC curves for soils with similar mineralogy, and even within the same soil type.

Table 2. Soil factors controlling swelling, dispersion and flocculation

Soil factors	Mechanism
1.Clay mineralogy and clay content	Charge originates in clay structures because of isomorphoussubstitution and broken bonds. Location of charge in tetrahedral structure is not available for hydration reactions. Thus, the total charge depends on the mineralogy and the amount of clay in soils.
2.Soil pH	Alters the charge on broken bonds by adsorption of H^+ or OH^- ions; With increasing concentration of carbonate anions, pH increases, and also negative charge on soil particles increases. When pH decreases, as observed in acidic soils, negative charge decreases.

3. Organic matter	Organic molecules bonded to clays by covalent bonding reducethe hydration charge of clay particles. Unbound, charged organic molecules can increase the hydration charge. Soil particles covered by hydrophobic organic matter are not affected by water interaction.
4. Inner sphere complexes	Cations such as Fe, Al, K fixed by clay minerals by inner sphere complexation (covalent bonding) reduces the hydration charge.
5. Cementation	Cementation of soil particles by Fe and Al oxides or calcium carbonate can block the charge available for water interaction.
6. Exchangeable cations	Exchangeable cations are attached to charged soil particles by a mixture of ionic and covalent bonding. The resultant ionicity of these bindings determines the net hydration charge. Dispersivecharge depends on the dispersive power of the exchangeablecations.
7. Electrolytes	Free (unbound) electrolytes in soil water contribute to the cationic flocculating charge which is a function of the flocculating power and the concentration of individual cations.

Thus these models based only on measures of sodicity and EC are not sufficient to explain all soil dispersive behaviour. Further, these models do not take into account the roles of K and Mg in influencing clay dispersion. Several researchers have shown the dispersive effects of K and also the less flocculating effect of Mg compared to Ca [e.g. 46, 25]. The use of EC (either as electrical conductivity of soil solutions or as total cation concentration) instead of the concentration of individual cations in these models neglects the fact that clay flocculation depends on the individual flocculating power of the cations involved [47, 48, 21]. For example, a given concentration of calcium has about 45 times more flocculating power compared to the same concentration of Na (see Equation 3). Another debate on the derivation of TEC centers on how much reduction in permeability or clay dispersion is permissible for different soil textures [11, 40].

3. Modification of TEC concept based on new insights

(i)Use of net dispersive charge to explain soil structural stability

As discussed in earlier sections, the new concepts of dispersive charge, flocculating charge and net dispersive charge lead to the re-definition of TEC as 'the flocculating charge estimated in flocculated soil suspensions (i.e. at the point of zero dispersion) where dispersive charge equals flocculating charge'. By determining these charges in a given soil eliminates the differences due to soil factors, detailed in Table 2. This new definition ends the current controversies reported in the literature on the effects of exchangeable cations, particularly K and Mg on soil structural stability [21]. Similarly, using the flocculating power of individual cations in determinations avoids the errors caused when electrical conductivity or total cation concentration is used to estimate TEC where all the cations are considered to be equal in the flocculation process.

Because of the role played by soil pH in determining the charge on particles, it is necessary to estimate the exchangeable cations and soluble cations at a given soil pH. However, it is very tedious to estimate exchangeable cations at a given soil pH. But, by using 1:5 soil water suspensions in flocculation experiments to measure flocculating charge, soil pH can be maintained. The procedure is essentially similar to the determination of 'dispersive potential' as described by Rengasamy2002 [47] and slightly modified by Marchuk and Rengasamy 2012 [48]. Known amounts of flocculants such as $CaCl_2$ are added to the dispersed suspensions step by step until complete flocculation is achieved.

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From the amount of $CaCl_2$ added and the concentrations of other cations in the original dispersed suspension, flocculating charge on soil basis can be estimated by using the Equation 3 for flocculating charge. If the addition of flocculants alter the pH of the suspension, pH adjustment may be needed.

(ii) Validity of models based on irrigation water quality

Some of the models [e.g. 9] based on TEC use the parameters such as SAR and EC measured in irrigation water to predict the effects of application of irrigation water on soil structural behaviour. But, it is well known that the effects of irrigation water on soil permeability and the reactions of irrigation water with soils such as adsorption of cations and solubility of soil constituents are influenced by several soil factors. As noted earlier, the changes in soil chemical and physical properties after treatment with irrigation water of a given quality are unique to each soil. Therefore, it is necessary to analyse the soils irrigated with a given water quality or the soils equilibrated with that irrigation water, so that the impact of irrigation water on soil structural stability can be established.

Irrigation waters commonly resourced from groundwater contain NaCl as the predominant salt. Hence, in earlier research, parameters such as SAR and ESP were central to determining effects on soil structural behaviour. SAR model, on the basis of 'Ratio Law' of Schofield [49], was developed to predict the adsorption of Na from soil solutions by charged particles. SAR of soil solutions is correlated with the ESP of soils, but the relationship varies with many soil factors. However, it has been commonly used to relate to clay dispersion instead of ESP because measurement of ESP is tedious and laborious. SAR is defined as:

$$\mathrm{SAR} = \mathrm{Na}/\ [(\mathrm{Ca} + \mathrm{Mg})^{0.5})] \qquad (4)$$

where concentrations of cations in soil solutions are expressed as mmol L^{-1}.

SAR does not include monovalent K and also treat Mg as equal to Ca. But recent use of waste waters and re-cycled waters have been shown to introduce significant amounts of K and Mg in addition to Na, and as discussed earlier K may influence soil structural stability and Mg effects may be different to those of Ca [50,51,52]. In view of this, Rengasamy and Marchuk 2011 [25] introduced a new index, the cation ratio for soil structural stability (CROSS) to relate to clay dispersion. CROSS takes into account the relative dispersive powers of Na and K, and also the relative flocculating powers of Mg and Ca. CROSS is defined as:

$$\mathrm{CROSS} = (\mathrm{Na} + 0.56\ \mathrm{K}) / [(\mathrm{Ca} + 0.6\ \mathrm{Mg})^{0.5}], \qquad (5)$$

where concentrations of cations in soil solutions are expressed as mmol L^{-1}.

Both CROSS and SAR are empirical properties. Relationship between SAR or CROSS and exchangeable cations may vary because many soil factors, including pH, affect exchange reactions, and hence, the dispersive charge. In spite of including K and Mg effects in the formula, the relationship between CROSS and clay dispersion or hydraulic conductivity, although stronger than SAR, has been found to vary with soil factors [52, 48, ,53, 54]. It is becoming clearer that clay dispersion in relation to CROSS depends on the dispersive charge of a given soil. The roles of clay mineralogy, organic matter, pH and other soil constituents in influencing charge available for water interaction are integrated in the concept of dispersive charge. Rengasamy *et al*. 2016 [21], using several soil samples with alkaline pH, have shown a significant correlation between dispersive charge of soils and CROSS of soil solutions. Further studies using various soil types are needed to investigate CROSS –dispersive charge relationship and to develop CROSS based models as guidelines for structural stability of irrigated soils.

4. Conclusions and future studies

Classifying irrigation water in relation to the impact on soil structural stability only on the basis of its ionic composition is not realistic, because the characteristics of the soil used for irrigation are also critical in the effects. The new concept of net dispersive charge influencing the degree of clay dispersion dispels the controversies surrounding the use of SAR (ESP) or CROSS and EC of soil

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solutions to explain structural stability of irrigated soils. Similarly, the debate on how much reduction in hydraulic conductivity or clay dispersion is to be considered to derive TEC is avoided by defining TEC as the flocculating charge at the point of zero dispersion which is an ideal condition for maintaining structural stability. The pH effect on dispersive charge is managed by measuring the flocculating charge in the soil-water suspensions at the given pH of the soil, thus avoiding the tedious determination of exchangeable cations.

As shown in Figure 2, when dispersive charge equals flocculating charge, clay dispersion is zero and physical properties of irrigated soils are not adversely affected. However, when the flocculating charge exceeds the threshold levels of crop tolerant salinity (measured as EC), crops are affected by osmotic stress and/or ionic toxicity. Then the soil becomes a 'saline' soil, but not dispersive. However, when the flocculating charge is less than dispersive charge, but at the same time the salt concentration is not tolerated by crops, the soil becomes 'saline-dispersive' with compounded effect of salinity and soil structural instability.

By conducting dispersion-flocculation experiments using a particular soil, the impact of irrigation water of known quality (in terms of composition of cations and anions) can be easily determined. If an irrigated soil remains flocculated, it indicates that the irrigation water contains cations at TEC levels and does not pose a threat to soil structure. But, the EC (salinity) effects on crops to be grown has to be determined for the successful use of that water. To avoid both these effects, the EC (due to NaCl) of irrigation water can be lowered and cations with high flocculating charge such as Ca^{2+} can be introduced. If a dispersive soil is flocculated by 0.1 M NaCl of an EC of 10 dS m^{-1}, the same can be achieved by 0.0022 M $CaCl_2$ with an EC of 0.22 dS m^{-1}. Alternative option could be appropriate leaching of salt (NaCl) in the field by improving leaching fraction and adding calcium compounds to soil such as gypsum to maintain structural stability. Ca^{2+} from gypsum application can reduce dispersive charge by reducing the levels of exchangeable Na and K, and also can increase the flocculating charge in soil solutions. The concept based on dispersive and flocculating charges can pave a way to identify innovative measures to reduce dispersive charge and increase flocculating charge of structurally degraded irrigated soils.

Jenkins and Morand 2004 [55], experimenting on acid-sodic soils (pH in water < 5.5) in New South Wales, Australia, concluded that relationships between clay dispersion, ESP, CEC and Al in these soils were complex and generally no trends were discernible. They also noted that ESP was a poor indicator of dispersive behaviour of acidic-sodic soils. In dispersive acidic soils, the role of pH, Al and Fe bound to clays in reducing dispersive charge and also the flocculating effects of ionic species of Al and Fe in soil solutions have not yet been investigated.

The current concept proposed in this essay has to be validated in all types of reclamation of salt-affected soils and in the application of poor quality irrigation water to soil. Laboratory determinations of TEC can serve only as guidelines for a soil irrigated with a specified water. Under field conditions, the chemical and physical effects of irrigation water can vary with several factors [e.g.2, 56, 57, 58, 59] such as drainage provisions, leaching fractions of soil layers, soil tillage conditions (cultivated vs no-tillage), and also methods of irrigation (flood irrigation, sprinkler or drip irrigation). Combining all these factors in the models, used for predicting the sustainability of irrigation, will be necessary to arrive at a practical approach to mitigate irrigation water effects on soil structure. However, frequent soil monitoring in the field after irrigation in conjunction with the laboratory derived parameters, and also evaluating the crop response in the field, can be useful in the management of irrigated soils. These approaches will be particularly important in land application of coal seam water and various other waste and recycled waters which are being promoted globally.

Acknowledgments: The author thanks the Grain Research and Development Corporation of Australia for the financial support (GRDC project UA 00159) and Dr Richard Greene of Australian National University whose comments improved the quality of this essay.

Conflicts of interest: The author declares no conflict of interest.

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