Soil-specific strategic irrigation: Saline-sodic water as an irrigation resource

A thesis submitted by

Aaditi Dang

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Dedication

To my grandparents,

Abstract

Declining water quality and quantity is a threat to the production of food and fibre worldwide. While irrigation using marginal quality saline-sodic (MQSS) water is emerging as a more common practice, it is still an under-utilised resource because of its potential detrimental impact on soil structure and crop production. The aim of the research was to enhance the current understanding of, and capability to, strategically utilise saline-sodic water as an irrigation resource through further investigation of the theory of threshold electrolyte concentration (C_{TH}).

Soil structural response to irrigation water quality is known to be a function of sodium (Na) contained in the irrigation water and the electrolyte concentration of that water. The C_{TH} is classically used to determine the suitability of water to be applied to a soil, and is usually conducted as a laboratory analysis utilising saturated hydraulic conductivity. This work aimed to validate the laboratory based semi-empirical disaggregation model approach to C_{TH} against field soils where MQSS water had been applied for an extended period of time. Unirrigated locations proximal to long-term irrigation sites were paired to provide control conditions. Results showed that the disaggregation model is useful for proactive planning of irrigation systems with regard to water quality and a good measure for identification of MQSS water as a strategic resource. The applicability of these results to irrigation guidelines was discussed with demonstrated a required focus on removal of generalised guidelines and identification of soil-specific tolerable hydraulic conductivity reduction.

The traditional method of determining C_{TH} is via leaching columns, which is a laborious and often expensive process Dispersive potential (P_{DIS}) was potentially a more rapid method which allowed determination of the C_{TH} in a practical sense, potentially providing a rapid means by which to make management recommendations for water quality use on a given soil. This work evaluated the P_{DIS} method against known C_{TH} data to determine the efficacy of use for non-dispersive soils irrigated with MQSS. Results suggest that the P_{DIS} approach to C_{TH} did not reliably, or efficiently, determine the C_{TH} in non-dispersive soils equilibrated with an irrigation solution.

The threshold used to define the tolerable reduction in hydraulic conductivity is generally the C_{TH} — defined as between a 10% and 20% reduction in saturated hydraulic conductivity from stable condition — others have suggested that the

aggregate-dispersion boundary may be used as this threshold instead. This boundary is also known as the threshold turbidity concentration (C_{TU}). Using a saturated hydraulic conductivity approach, this work sought to quantify the extent of reduction at the C_{TU} and compare this to traditional C_{TH} approaches. It was found that saturated hydraulic conductivity reduced between 44 and 78% for the five Vertisol soils investigated. This indicated that the C_{TU} varied between soils and was substantially more than the 10–20% reduction in hydraulic conductivity at the C_{TH}. Quantification of this boundary condition allows more sensible selection of tolerable K_{sat} reduction that does not result in undue irreversible structural decline.

Use of non-traditional irrigation sources will increase, with many industry wastewaters containing potassium. Potassium is known to result in soil structural decline if the concentration of K is sufficient. Current approaches to determining C_{TH} do not incorporate K. This work sought to investigate incorporation of K into the disaggregation model for C_{TH} and validate this against an equivalent Na systems using an ionicity approach. It was found that a single generalised coefficient of equivalence for K relative to Na does not appropriately describe the system changes, rather that this coefficient specific to a soil and appears to vary with the percolating electrolyte concentration. Incorporation of K into the disaggregation model, while not accurate with a universal coefficient of equivalence for K, was considered reasonable where no other approach could be used. This conclusion was drawn on the basis that the model would serve to produce a conservative C_{TH} under such circumstances, which would not cause undue degradation to the soil environment.

Relating the reduction in net negative charge to the rK_{sat} was hypothesised to provide vital information concerning soil-specific reduction rates. The net negative charge, measured as zeta potential (ζ), was determined for three soils of distinct difference. The disaggregation model approach to C_{TH} was used to determine rK_{sat} with ζ measured at each treatment solution in the C_{TH} methodology. Zeta potential was found to be a function of SAR and EC for a given pH with a general equation provided. Net negative charge and rK_{sat} were very highly related (R^2>0.8 for all three soils), although the slope of the relationship was distinctly different for the three soils, in keeping with literature describing the influence of clay content and oxide content on the reduction in hydraulic conductivity. Additional research into the effect of clay content,

sesquioxide occurrence and ζ on rK_{sat} is required to use ζ for prediction, but this work showed promise in moving towards a predictive model.

This research clearly established the feasibility of strategic MQSS water usage, but also identified several impediments in its use with reference to the soil-specific response, the methodology used to determine the suitability, the presence of magnesium (Mg) and potassium (K), the mechanisms controlling the soil response, and finally the guidelines used to determine the suitability.

Certification of Thesis page

This thesis is the work of Aaditi Dang except where otherwise acknowledged, with the majority of the authorship of the papers submitted undertaken by the Student. The work is original and has not previously been submitted for any other award, except where acknowledged.

Principal Supervisor

Associate Professor John McLean Bennett

Associate Supervisor

Dr Alla Marchuk

Associate Supervisor

Dr Andrew Biggs

Student and supervisors signatures of endorsement are held at USQ.

List of publications submitted from this thesis

Throughout the course of this candidature the first four experimental chapters have been submitted to peer reviewed journals, as indicated below. Chapter 7 has not been submitted prior to thesis submission.

Chapter 3

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Contributor	Statement of contribution
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Author 3 Dr Alla Marchuk	Conception and design (10%) Analysis and interpretation (5%) Drafting and production (5%)
Author 4 Dr Serhiy Marchuk	Analysis and interpretation (5%) Drafting and production (5%)
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Author 2 Associate Prof John McLean Bennett	Conception and design (30%) Analysis and interpretation (15%) Drafting and production (15%)
Author 3 Dr Alla Marchuk	Conception and design (20%) Analysis and interpretation (15%) Drafting and production (15%)
Author 4 Dr Andrew Biggs	Conception and design (5%) Analysis and interpretation (5%) Drafting and production (5%)
Author 5 Prof Steven Raine	Conception and design (5%) Analysis and interpretation (5%) Drafting and production (5%)

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Author 2 Associate Prof John McLean Bennett	Conception and design (20%) Analysis and interpretation (20%) Drafting and production (20%)
Author 3 Dr Alla Marchuk	Conception and design (20%) Analysis and interpretation (10%) Drafting and production (5%)
Author 4 Dr Andrew Biggs	Conception and design (5%) Analysis and interpretation (5%) Drafting and production (5%)
Author 5 Prof Steven Raine	Conception and design (5%) Analysis and interpretation (5%) Drafting and production (5%)

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Author 3 Dr Alla Marchuk	Conception and design (10%) Analysis and interpretation (5%) Drafting and production (5%)
Author 4 Dr Serhiy Marchuk	Analysis and interpretation (5%) Drafting and production (5%)
Author 5 Dr Andrew Biggs	Conception and design (10%) Analysis and interpretation (5%) Drafting and production (5%)
Author 6 Prof Steven Raine	Conception and design (10%) Analysis and interpretation (5%) Drafting and production (5%)

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Abbreviations and acronyms used

C_{TH}	Threshold electrolyte concentration (TEC)
C_{TU}	Threshold turbidity concentration
CEC	Cation Exchange Capacity
CFC	Critical Flocculation concentration
CROSS	Cation Ratio of Soil Structural Stability
DI	Deionised Water
DDL	Diffuse Double Layer theory
EC	Electrical Conductivity
ESP	Exchangeable Sodium Percentage
ECR	Exchangeable Cation Ratio
EDP	Exchangeable Dispersion Percentage
FC	Flocculation Concentration
Fit Std	Error Standard Error Coefficient
ICP- MS	Inductive coupled plasma atomic mass
k	Soil Permeability
k_{sat}	Saturated hydraulic conductivity
LF	Leaching Fraction
MQW	Marginal Quality water
MQSS	Marginal Quality Saline-Sodic water
PZNC	Point of Zero Net Charge
PAR	Potassium Absorption Ratio
P_{dis}	Dispersive Potential
SAR	Sodium Adsorption Ratio
TDS	Total Dissolved Solids
TC	Turbidity Concentration
TCC	Total Cation Concentration

1 Introduction and overview

1.1 Introduction

Water, alongside soil, is considered as one of the two most important resources for sustaining ecosystems. The irrigation sector claims about 70 percent of the freshwater withdrawals (Renner 2012). In 2009, the United Nations Food and Agriculture Organization (FAO) found that globally 311 million hectares were equipped for irrigation but only 84 percent of that area was actually being irrigated (Renner 2012) due to unavailability of the resources. It is apparent that irrigation is a majority user of water, but there will be competing priorities for fresh-water resource leading to a greater importance of poorer quality water as a resource. Unfortunately, the pressure placed on fresh-water resources creates a requirement for poorer water quality use in agriculture industry. There is also an associated pressure to address food/fibre demands in water limited environments where marginal quality is the only resource available (Qadir et al. 2007a). Where the use of poor quality water has not been well guided/regulated, or only recently acknowledged, there is an associated decline in soil as a receiving environment, and a decline in the quality of freshwater worldwide due to mixing of run-off waters and groundwater recharge. Hence, the use of marginal and poor quality water presents as a vital management issue.

Irrigation in Australia has been developed over a wide range of climatic zones including semi-arid, temperate, tropical and subtropical climates. In Australia, irrigation commenced in the 1880s and has expanded from an area of 50,000 ha in 1904–09 to 1.84 million hectares in 1991 (Rengasamy & Olsson 1991), using 10.2 million ML of water annually (National Irrigators' Council 2009). The value of irrigated agricultural production in Australia has exceeded $15 billion (Australian Bureau of Statistics 2016). Australia has 61 major groundwater provinces (Plazinska 2007), with irrigation as the main use of groundwater, specifically for Queensland, where 46% of total irrigation uses groundwater. In 2008–09, an estimated 15,077 agricultural business in the Murray–Darling Basin used water for irrigation (Ashton et al. 2011). These statistics show a heavy reliance on water resources for irrigation, and the reliance on irrigation for agricultural production is not set to decline (de Fraiture et al. 2007).

Irrigation with the use of marginal quality water is a growing practice, globally. The term ‘marginal-quality waters’ refers to water that may contain one or more impurities at levels higher than in freshwater, including salts, metals, metalloids, residual drugs, organic compounds, endocrine-disrupting compounds, and the active residues of personal care products and/or pathogens (Qadir & ChoukrAllah 2013). Most of the marginal quality water used in irrigation today stems from wastewater. In the context of this study, the term ‘marginal quality water’ refers to saline-sodic (MQSS) water, where water quality parameters to assess this are contained in Australian and New Zealand guidelines (ANZECC 2000). The International Water Management Institute estimated that wastewater has been used to irrigate over 4–6 million hectares (Scott et al. 2010). However, MQSS water is typically avoided as it is viewed as detrimental to soil structure and agricultural production, while recent research suggests that such water can be used strategically, which means this potential resource is under-utilised (Beltrán 1999).

The cotton industry is essential to many regional communities in Australia within Queensland and New South Wales (NSW). The Australian cotton crop was estimated at $1.3 billion during 2014–15 (Cotton Australia 2016). The industry has a significant water requirement, with the volume of irrigation water applied in cotton representing 24% of the national irrigation water usage. On an average, cotton requires about 7.8 ML/hectare of irrigation. In recent years (from 2000–01 to 2009–10), the irrigation water index for Australian cotton growers has doubled from 1.1 bales/ML to 1.9 bales/ML (Cotton Australia 2016). This creates a need to explore an alternate more readily available resource such as MQSS.

The MQSS water is currently viewed as detrimental to cotton production and soil structure, resulting in underutilisation of this potential resource. Given the fact that Australia regularly experiences drought conditions, and is documented as having depleting water resources, research into potential use of MQSS water is crucial (Qadir et al. 2007b). Rapid development of the coal seam gas (CSG) industry throughout eastern Australia has also raised interest in the use of saline-sodic groundwater produced as a CSG by-product, as an irrigation resource (Bennett & Raine 2012; Bennett et al. 2016b). Furthermore, where this water occurs within in agricultural production regions, including Broadacres grains and pulses, and fibre crops such as cotton, there is enhanced interest in its utilisation. The quality of groundwater used for

irrigation, and overland flow with appreciable salts, (Biggs et al. 2013; Biggs et al. 2012) is not dissimilar to CSG water after treatment (Bennett et al. 2016b). Subsequently, both require management and consideration in line with current CSG industry beneficial use regulations. Since the impact of MQSS water on soil permeability is site-specific (Bennett & Raine 2012; de Menezes et al. 2014; Marchuk & Rengasamy 2012; McNeal & Coleman 1966), risk of structural failure of the soils where this water is being used needs to be considered.

Soil structure is a soil-specific function of electrolyte concentration (measured as electrical conductivity; EC) and sodium adsorption ratio (SAR), which is the measure of salinity and sodicity determined in solution, respectively. As EC declines while SAR remains static, the soil structure deteriorates. Similarly, for static EC while SAR increases (Sumner 1993). A proximal measure of soil structural dynamics is the change in saturated hydraulic conductivity from a baseline condition. A negative change in water quality (reduction in EC and/or increase in dispersion inducing cations), can cause deterioration in structure leading to decreased soil pore diameter and frequency (Frenkel et al. 1978) . In terms of representation of the baseline condition, Quirk and Schofield (1955) suggested that a calcium (Ca) dominant environment induces a potential minima where small changes in energy do not lead to changes in structural condition between Ca-saturated clay quasi-crystals. The point of potential minima with no structural changes can be termed as absolute stability of a soil (Bennett et al. Submitted). A measureable reduction in soil hydraulic conductivity (10–25% reduction) from absolute stability for a given SAR, is referred to as the threshold electrolyte concentration (C_{TH}) (Ezlit et al. 2013; McNeal & Coleman 1966; Quirk & Schofield 1955; Raine et al. 2007). In this respect, the C_{TH} as a specific value of departure from absolute stability is somewhat arbitrary. Due to introduction of sodium (Na) to the system, the potential minima is overcome and the hydraulic conductivity declines. However, measurement/calculation of such a threshold needs to exist outside the source of measurement error, which is why a reduction in saturated hydraulic conductivity (rK_{sat}) of 20% was used by Ezlit et al. (2013). Importantly, Quirk (2001) explained that the reduction at this point is due to swelling within clay quasi-crystals and the development of diffuse double layer between quasi-crystals, rather than dispersion of clay particles. Others maintain that the threshold between aggregation and dispersion conditions should be defined as C_{TH}. However, in this work the

definition presented in Ezlit et al. (2013), based on Quirk and Schofield (1955)'s concept, is maintained and the practical significance of using this threshold over that of the aggregation–dispersion boundary is investigated.

The SAR and exchangeable sodium percentage (ESP) are used as the traditional indicators for soil sodicity and the effects of Na on soil structure to soil solution and soil solid phases, respectively. Thus, methods for the determination of C_{TH} have focussed on these parameters (Ezlit 2009). Sodic water is defined as having a SAR greater than 12 (ANZECC 2000). However, the presence of potassium (K) and magnesium (Mg) within soils is known to have differential effects on soil dispersion and flocculation as compared to Na and Ca, respectively. Due to this, the cation ratio of soil stability (CROSS) is currently considered as a superior alternative to SAR as an index of soil structural stability from the perspective of water suitability for irrigation (Rengasamy & Marchuk 2011). Furthermore, Bennett et al. (2016a) proposed the use of exchangeable dispersion percentage (EDP) as an index for analysing exchangeable cations as a superior index to ESP. Consideration of cations other than Na within waters is therefore required.

Traditional approaches to measuring C_{TH} utilise SAR, but they do not include the potential effects of K and Mg. For this reason, Marchuk and Rengasamy (2012) and Rengasamy and Marchuk (2011) investigated C_{TH} and dispersive potential in relation to CROSS to include the effects of the full cation suite as a direct measure of clay dispersion in water. However, due to the limited number of soils used in their studies, a robust relationships between C_{TH} and CROSS needs to be further investigated using a larger number of soils with different properties, especially in relation to smectitic soils such as Vertosols (IUSS Working Group 2014) in cotton growing areas of Queensland and NSW.

Dispersive potential as described by Rengasamy (2002), provides an indication of the Ca requirement to maintain flocculation of a dispersed clay colloidal suspension. It describes the boundary between the aggregated and dispersed state of soil. However, it does not directly measure C_{TH} as described by Ezlit et al. (2013) in terms of rK_{sat}=20%, or indeed in any terms of hydraulic conductivity. According to Quirk and Schofield (1955), the aggregation–dispersion boundary is defined as the threshold turbidity concentration (C_{TU}), where dispersed clay first appeared in leachates of soil

columns subject to solute percolation. Quirk (2001) demonstrated that the C_{TU} is effectively equivalent to the point of spontaneous dispersion for sodic soils and that the C_{TH} was 3–4 times the concentration of the thresholds associated with C_{TU}. Dispersive potential is further based on the concept of a cation's ability to induce covalent bonds, which is stronger than short-range Van Der Waals attractive forces that generally dominate soil stability. The definition of C_{TH} used in this work does not directly account for this (Bennett et al. Submitted; Quirk 2001). Hence, there is merit in investigating both the dispersive potential and traditional C_{TH} determination methods for further understanding the mechanisms and dynamics of soil-specific response. Understanding the differences between these two approaches provides further information in terms of practicality of application. This requires further examination as the cost of C_{TH} analyses using the semi-empirical approach of Ezlit et al. (2013) is prohibitive to its general use in agriculture (~AUD$3,000 per soil), primarily due to it being a labour-intensive methodology.

Industry currently operates on the basis of a general guideline (ANZECC 2000) as a broad-brush, blanket approach, rather than a strategic approach whereby soil tolerance is matched to water quality through semi-empirical predictions. Application of MQSS water on a strategic basis is possible if a model can be developed to allow prediction, or if the soil-specific C_{TH} is directly measured as has been done in the Australian coal seam gas industry (Bennett et al. 2016). Identification of this basis will be important to the sustainability of irrigation industries in the face of competing pressures on global freshwater resource. Simplifying the means to measure soil-water interactions on a soil-specific basis will promote wide-scale adoption of sustainable land use practices, increase soil stability and productivity and promote sustainable technologies aimed at optimising economic development.

1.2 Aims and objectives

The C_{TH} concept has demonstrated that soils respond differently to MQSS (Bennett et al. Submitted; Bennett & Raine 2012), thus making the direct prediction of this soil-specific response very useful. While the C_{TH} is represented as a measureable arbitrary reduction in soil hydraulic conductivity, the pressures defining clay separation, due to numerous inherent soil characterise (e.g. clay content, organic matter, carbonates and oxides etc.), vary for this common reduction (Bennett & Raine 2012; Ezlit et al. 2013; Marchuk et al. 2013a). This thesis attempts to move forward an examination of the

requirement to understand the reasons for a soil-specific response in moving towards predictive approaches.

Quirk and Schofield (1955) approach measures the C_{TH}, which differs from the C_{TU} measured by dispersive potential (Rengasamy 2002). Understanding the extent of differences between these two parameters may reveal important information about dispersion dynamics, and it also serves to identify and explore the practicality of irrigation with MQSS water in terms of irreparable damage and rK_{sat}. Additionally, for both the approaches, the assessment is laboratory based and the timescales of effect to reach chemical equilibrium for *in situ* soils is postulated to be much greater than for laboratory results (Oster & Shainberg 2001). Therefore, it is useful to understand the validity of the C_{TH} approach for field irrigated soils in terms of practical irrigation guidelines.

Recent advances in the variable effects of cations on dispersion and flocculation (Arienzo et al. 2009; Rengasamy & Marchuk 2011; Smith et al. 2015) requires that incorporation of K and Mg to be considered in terms of assessing soil C_{TH}. However, the role of Mg in terms of dispersion is still contentious and requires further investigation beyond the scope of this thesis. On the other hand, Bennett et al. (2016a) suggest that EDP is equivalent to ESP, and that the inclusion of K in this index significantly improved the explanation of variability in dispersed clay. This suggests merit in investigating the inclusion of K into C_{TH} traditional measures.

Finally, the cost of determining C_{TH} in the laboratory is prohibitive on an agricultural industry scale, resulting in potential under-utilisation, or inappropriate utilisation, of MQSS water as a strategic resource under current guidelines (ANZECC 2000). While this thesis seeks to contribute towards prediction of soil-specific response, it is likely that truly useful pedotransfer functions describing soil-specific functions will not be attainable in the direct short-term. Thus, the identification of simplified methodologies will be a contextual focus of the general discussion of the findings within this thesis. Such discussion endeavours to drive short-term implementable solutions where the development of a pedotransfer function is not possible.

The **principal aim** of this research is to enhance the current understanding of, and capability to strategically utilise saline-sodic water as an irrigation resource through further investigation of the theory of C_{TH}. This research further seeks to understand the

mechanisms for soil-specific response to irrigation water quality, with a focus on net negative charge in order to provide the cotton industry with proximal variables that could potentially be used to estimate C_{TH}, or soil dispersive potential parameters. Therefore, this work has the following **objectives**:

Objective 1: Validate the current C_{TH} methodology for irrigated soils under current industry management with MQSS water

Objective 2: Compare *dispersive potential* and C_{TH} in terms of semi-empirical calculations for soil susceptibility to dispersion for a given water quality, with practical management of irrigated soils as the focus

Objective 3: Incorporate [K^+] dispersive effects into a disaggregation, semi-empirical model based on saturated hydraulic conductivity

Objective 4: Investigate the controlling mechanisms for both C_{TH} and dispersive potential to enhance predictive output and subsequent irrigation advice

1.3 Thesis overview

As this thesis has been prepared with each chapter as a standalone section of the main body of work, with 4 of the 5 experimental chapters with peer reviewed journals for consideration, the presentation of a combined methodological chapter has been avoided. Each chapter provides the detail necessary to repeat and understand the work contained within it. With that said, the following provides overview of the thesis structure:

Chapter 1: Introduction and overview

This chapter introduces broad issues associated with the use of MQSS water for irrigation and associated effects on the soil resource. It identifies various questions pertaining to the complex nature of management for sodic soils and introduces the aims and objectives of the study in relation to these.

Chapter 2: Saline-sodic water as a strategic irrigation resource- A review

This chapter presents the background information that pertains to the current research and highlights knowledge gaps that further reinforce the justification for this study. This chapter covers: (i) the justification and necessity to use MQSS water, (ii) factors that affect a soil's structural stability, (iii) the current theories used to analyse soil's

response to a certain water quality, (iv) the potential changes that occurs in soil due to the presence of K and Mg, (v) a scrutiny into the impacts of these changes to the current guidelines, and (vi) finally examining the prospect of predicting the response of a soil to a certain water quality. This review therefore, details and critically synthesises the relevant information and identifies knowledge gaps in the safe utilization of MQSS water for irrigation.

Chapter 3: Validating laboratory assessment of threshold electrolyte concentration for fields irrigated with marginal quality saline-sodic water

This chapter focuses on validating the rK_{sat} predictions obtained by semi-empirical modelling of C_{TH} in the laboratory and compare with field-equilibrated samples and their associated rK_{sat} observations. The chapter also details a methodology to make the assessment for cultivated agriculture, where soil pore networks are disturbed.

Chapter 4: Evaluating dispersive potential to identify the threshold electrolyte concentration in non-dispersive soils

This chapter presents an investigation into the capability of dispersive potential as a soil specific determination of C_{TH} in Vertosols. The practicality of dispersive potential as a method is subsequently critically analysed and limitations of dispersive potential approaches are examined in detail.

Chapter 5: Quantifying the aggregate-dispersion boundary condition in terms of saturated hydraulic conductivity reduction and the threshold electrolyte concentration

This chapter investigates the concept of reparable rK_{sat} prior to breach of the aggregate–dispersion boundary, defined as the C_{TU}. The aggregate-dispersion boundary has been suggested as the threshold for application of marginal quality water. The rK_{sat} at the C_{TU} is related to the C_{TH} for the same soils to examine if there is a constant relationship between these thresholds as assumed or if the relationship varies between soils. This will help decipher if the management guidelines need to be changed to work with C_{TU} rather than C_{TH}.

Chapter 6: Towards incorporation of potassium into the disaggregation model for determination of soil-specific threshold electrolyte concentration

This chapter focuses on the incorporation of K into the disaggregation model through the utilisation of a K coefficient of equivalence in terms of Na's propensity to induce dispersion. While the importance of including K in the model is demonstrated, use of a universal coefficient of equivalence is questionable.

Chapter 7: Reduction in saturated hydraulic conductivity as related to the net negative charge of clay

The net negative charge was a consistently important feature that appeared to transcend both traditional C_{TH} and dispersive potential approaches. This chapter investigates combining rK_{sat} approaches with the iconicity concept to describe soil-specific response in terms of the electrophoretic mobility of clay particles. The limitations of measurement methods were identified and subsequently discussed.

Chapter 8: General Discussion, Conclusion, and Future Work

This chapter synthesises the various findings of the various experiments and discusses these in terms of the overarching aim, through the specified objectives. Concerted focus is provided on how the thesis outcomes provide practical insight for the use of MQSS water for irrigation, and its potential to shape irrigation guidelines and best management practices. Conclusions are subsequently drawn from this work, and recommendations for future work are made.

2 Saline-sodic water as a strategic irrigation resource- A review

2.1 Introduction

A rapid growth in population and residential creep has resulted in greater demand for food and fibre. This has caused a growing pressure on the agricultural industries to produce at a greater rate with a lesser number of available resources. A study conducted by Wild (2003) predicted that global food production will need to increase by 38% by 2025 and by 57% by 2050 to ensure that there is a match between the supply and demand. Given the finite amount of arable land, and its continued decrease due to urban pressures, this equates to demand for increased production per unit of land (Lawrence et al. 2013). Irrigation supplements the water requirement of plants, reduces stress and maximises production, resulting in greater production efficiency per unit area of land. However, irrigation area cannot increase unless greater freshwater resource is made available, or an alternate water source is provided, which is more likely for lower quality waters (Qadir et al. 2007b). In the first instance, this means that irrigation industry needs to be exceptionally resource efficient to increase production per unit land area without increasing the water resource, although there are many threats to the viability of freshwater irrigation resources (Howell 2001). Hence, an alternate water source will be vital to the longevity and expansion of irrigation, while efficiency must still be focussed on (Raine et al. 2007). Secondly, in some parts of the globe, where proximal agricultural production is currently difficult, there is only access to marginal quality saline sodic water (Qadir et al. 2007b). In such circumstances it is vital that management practices are well informed on a soil specific basis.

Water quantity and water quality degradation are global concerns that will intensify with increasing water demand, the unexpected impacts of extreme events, and climate change in resource-poor countries (Qadir et al. 2007b; Watson et al. 1998). Worldwide, marginal-quality water is becoming an increasingly important component of agricultural water supplies as an alternate water resource, particularly in water-scarce countries (Qadir et al. 2007b). However, there are concerns in the use of such water, particular in terms of decrease in soil permeability caused by MQSS water via the high concentrations of cations, the potential for monovalent cations to dominate this

concentration, the propensity of MQSS water to be associated with alkalinity, and long term accumulation of all of these (Aylmore & Quirk 2013; Grattan & Oster 2003; So & Aylmore 1993). Therefore, while MQSS water offers a possible alternate irrigation resource and there is increased pressure to use it, there are also a series of environmental principal concerns that must be addressed.

Soil structural stability describes the ability of the soil to retain its arrangement of soil and pore space when exposed to external forces and it is key to ensuring adequate root exploration of the soil profile (Gliński & Lipiec 1990). Roots tend to utilise existing pores rather than create their own, for the majority of the root distribution of broad acre crops and pastures. The stability of effective pores depends on the stability of soil aggregates and the strength of bonds between soil structural units (Marchuk et al. 2013b; Nelson & Oades 1998; Quirk & Murray 1991). Soil structure can be influenced by many factors such as clay content (Frenkel et al. 1978), clay mineralogy (Churchman et al. 1993), exchangeable cations (Sumner 1992), soil pH (Chorom et al. 1994), electrolyte concentration (Quirk & Schofield 1955), organic matter (Tisdall & Oades 1982), carbonates (Chorom & Rengasamy 1997) and oxides (Goldberg 1989). It stands then that soil structural stability is an inherently complex factor to understand in terms of the mechanism responsible for dynamic changes at any point in time.

Quirk and Murray (1991) present a scheme showing the interrelationship of soil structural behaviours and the research areas that investigate these. They split these behaviour into macroscopic (slaking and deflocculation/dispersion) and microscopic (interparticle forces, particle distances, and physical swelling and water relations of clays). Quirk (2001) suggested that the order of operations in terms of hydraulic reduction was firstly contingent on factors affecting microscopic behaviour and then those affecting macroscopic behaviour.

Tisdall and Oades (1982) explain the importance of the soil organic fraction on soil aggregate stability from the nano-scale through to the macro-scale. Although, Bennett et al. (Submitted) observed that microscopic behaviour was not affected by organic matter, suggesting that the organic fraction, while present at the scale of operation for microscopic behaviour, was not sufficient in bonding strength to be important until macroscopic behaviours were approached. Therefore, understanding the microscopic

behaviour of soil structure and the factors controlling it, will be fundamental to identifying soil-specific rK_{sat}.

Quirk and Schofield (1955) stated that the C_{TH}, a function of EC and SAR, is the principle factor controlling the microscopic behaviour dynamics within a soil, and that the clay mineralogy presents the greatest influence on soil-specific behaviour between soils. The premise of their work is that a soil is demonstrated to be in a potential minima when saturated with Ca, and small changes in energy (solution concentration) from this point do not result in hydraulic decline, but introduction of Na to the system results in a gradual hydraulic decline from this absolute stability (i.e. potential minima). Therefore, the C_{TH} represents a measureable departure from absolute stability beyond the error associated with the measurement method, and is defined as the EC for a particular SAR at rK_{sat}=20% (Ezlit et al. 2013). At this point, the clay quasi-crystal (ordered clay structure) has undergone intracyrstalline swelling (smectites) and intercrystalline swelling, which occurs for non-smectitic minerals also (Murray & Quirk 1990; Quirk & Aylmore 1971), due to the development of a diffuse double layer (Quirk & Marcelja 1997). The separation of clay particles occurs in the order of angstroms ($1/10^{th}$ of a nano-meter), but results in rK_{sat}=20% prior to dispersion occurring at the aggregate–dispersion boundary, or C_{TU}. Hence, Bennett et al. (Submitted) refer to the expansion of the clay domain (intracystalline and intercrystalline swelling) approaching the C_{TU} as the disaggregation process, to conceptually separate the microscopic behaviour of clay domain swelling from the macroscopic behaviour of dispersion. Whilst clay mineralogy is generally thought to control the soil specificity of the C_{TH}, we currently cannot predict its occurrence, implying that further work is required to determine this microscopic behaviour.

Rengasamy and Sumner (1998) introduced the notion that the ionisation potential of the various cations contained in the soil solution are important to the microscopic behaviour of soil structure. The ionisation potential also defines the propensity of the cation suite to develop covalent bonds. The importance of covalency in determining structural stability of clays prior to dispersion was further confirmed by Marchuk et al. (2013b). To date, there has not been any work seeking to combine the ionisation potential and clay domain concepts to describe the microscopic behaviour of soil structure. Therefore, there is merit in investigating approaches that utilise this theory,

such as dispersive potential (Marchuk & Rengasamy 2012; Rengasamy 2002), and evaluating these with respect to C_{TH} methods based on rK_{sat}.

In the past, only Na concentration was used to examine the potential for water infiltration to result in hydraulic decline (Arienzo et al. 2009). Therefore, the current irrigation guidelines only consider the SAR, and exclude the full cation suite as affecting soil structure (ANZECC 2000). The physical and chemical properties of a soil are greatly influenced by the cation suite (Ca, Mg, K and Na) present in the soil/water systems (Rengasamy & Marchuk 2011). Potassium affects the dispersive likelihood of a soil, while Mg predominately contributes to flocculation potential of a solute. Thus, there is a need to reconsider current guidelines used for irrigation management, especially as the requirement to irrigate with MQSS water increases.

This review seeks to investigate (i) the potential use of MQSS water for irrigation, (ii) the factors controlling soli structural stability, (iii) examination of the methodology to analyse the soil response to saline-sodic water for irrigation, (iv) the effect of K and Mg on soil stability (v) analysis of current guidelines for the use of saline-sodic water for irrigation, and (vi) basic analysis of the available modelling software that could enable a prediction of C_{TH}.

2.2 Marginal quality saline-sodic water

Use of MQSS water is often not considered, due to a concern about the decrease in soil permeability. MQSS water can have high concentration and unfavourable cation suite, meaning that the long term application of such wastewaters will affect the levels of both soluble and exchangeable cations and lead to soil structural deterioration and salt accumulation in the soil (Bennett et al. 2016a; Rengasamy & Marchuk 2011). If such water is to be used strategically, then long-term impacts on crop growth and yield in terms of the soil-water-plant system need to be considered. This section firstly defines MQSS water in terms of this thesis, acknowledging that the water suitability is also hinged on soil-specific response, and discusses the intentions of strategic use, and then considers situations where production is reliant on MQSS water.

2.2.1 Defining marginal quality water

The potential for soil structural degradation and adverse crop conditions due to irrigation is contingent on the quality of the water. In general, as the water quality becomes more sodic, the soil structure declines and the soil macropore volume is

decreased rapidly (Marchuk & Rengasamy 2012). As the water becomes more saline, soil structure can be improved due to osmotic compression of repulsive forces governing soil structure, but the productivity of crops is reduced (Russell 1976; Zhang et al. 2010) determined by the crop salinity tolerance (Ayers & Westcot 1985). When the irrigation water percolates through soil profile, the soil solution composition is significantly altered through cation and anion exchange, ion complexion, formation of different ionic species and precipitation of compounds dictated by solubility criteria (Figure 2.1).

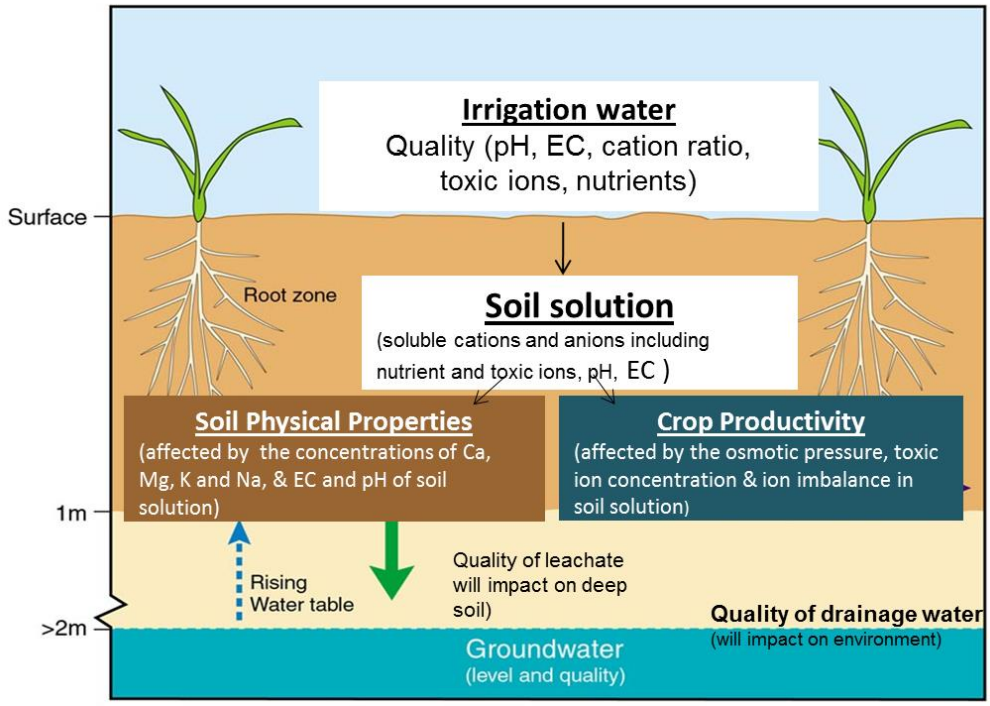

Figure 2.1. Quality of irrigation water affects the soil solution composition subsequently affecting soil physical properties and crop productivity (Rengasamy 2002, 2006).

Suitability of saline water for irrigation depends primarily on the kind and amounts of salts present, the soil type in question, specific plant species and growth stage and the amount of water leached beneath the root zone, or the leaching fraction (LF) (Bauder et al. 2008; Rhoades 1988; Van Hoorn 1981). The nature and concentration of cations and anions in soil solution affects soil structural stability and associated soil physical phenomena (Marchuk et al. 2013a; Rengasamy 2010; Rengasamy & Churchman 1999). Although both monovalent Na and K have been found to adversely affect soils, the land managers' current focus is only on Na. Continuous use of saline-sodic irrigation water might lead to accumulation of salt above the threshold level of crops.

Low water salinity and high levels of sodicity can cause soil degradation and reduction in soil permeability (Ezlit et al. 2010). Such degradation results in aeration and waterlogging problems which negatively affect the crop yield. Consequently, waterlogging and low permeability might also induce salt accumulation within the root zone (Ezlit et al. 2010). Therefore, awareness of the properties of the saline water and soil in question as the level of effect will vary depending on the salts, soils, and the leaching fraction (LF) is imperative. The soil structure degradation due to rising sodicity is unique for a given soil and its condition (Evangelou & McDonald Jr 1994; Ezlit et al. 2010). Determining the sodicity effects within a given soil requires a comprehensive knowledge of the mineralogy, structure and chemistry of that soil (Rhoades et al. 1999). The time required to develop sodicity and salinity problems can be determined by the sodicity and salinity levels in irrigation water, along with management practices.

As there is no universal definition of 'marginal quality' water, for the purpose of this review, it has been broadly defined as: water that possesses certain characteristics which have the potential to cause problems when it is used for irrigation. A strict definition is contingent on the soil response, so the definition provided here is only meant as a guideline. There are two major types of marginal-quality water: wastewater from urban and peri-urban areas, and saline and sodic agricultural drainage water and groundwater. This project has a specific focus on Marginal Quality Saline-Sodic water.

2.2.2 Current guidelines in place for the use of marginal quality water

There are many different guidelines available to ensure that marginal quality water can be used safely and productively (World Health Organization 2006). These guidelines are created from water quality parameters stemming from different waters.

The current ANZECC (2000) guidelines for irrigation water quality are based on the C_{TH} concept of Quirk and Schofield (1955). The ANZECC (2000) guidelines do not stipulate a reduction in K_{sat} from the stable condition to determine a soils' individual C_{TH}, instead they refer the reader to a graph with two curves representing soil in stable and non-stable conditions (Figure 2.2) to determine whether or not a water quality is safe for use. As there are very few examples of C_{TH} relationships found in the published literature, these guidelines for water quality are commonly used to determine the

appropriate selection of saline-sodic water to maintain soil permeability. The guidelines state:

> *"Evaluate the quality of the irrigation water by superimposing its ECi [electrical conductivity of irrigation water in dS/m] and SAR [sodium adsorption ratio] values on the graph (ANZECC 2000) to see if it will affect soil structure (through clay aggregate breakdown). Water quality that falls to the right of the dashed line is unlikely to cause soil structural problems. Water quality that falls to the left of the solid line is likely to induce degradation of soil structure; corrective management will be required (e.g. application of lime or gypsum). Water that falls between the lines is of marginal quality and should be treated with caution."* (ANZECC 2000)

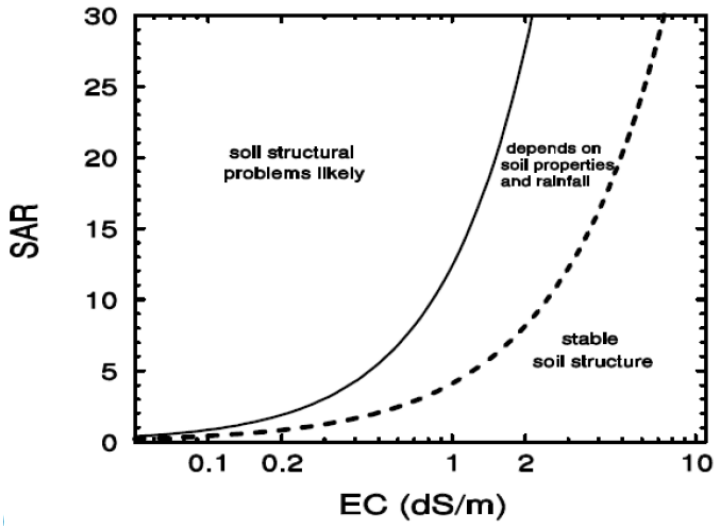

Figure 2.2. Relationship between SAR and EC of irrigation water for prediction of soil structural stability (ANZECC 2000).

Whilst these guidelines have been adequate in seeking to assist management, they can be improved to allow a soil-specific management strategy.

2.2.3 Strategic irrigation considerations

Irrigating successfully with saline or sodic water requires careful management to prevent short-term reduction in crop yield and long-term reduction in productivity. When wet, dispersive soils can undergo a deterioration in soil structure, due to the dislocation of clay from aggregates (Rengasamy & Olsson 1991, 1993). Farmers using saline water must manage irrigation carefully to minimize potential losses due to crop sensitivity to salinity, chloride toxicity, nutrients deficiencies, and structural deterioration of soils (Ayers & Westcot 1985). Poor water storage and restricted water and air movement in the soils, due to saline water usage, need to be considered along

with the impact on germination, root growth and water use efficiency (Rengasamy & Olsson 1991). The management options include leaching for salinity control, amelioration to manage the increasing levels of sodicity, along with crop selection (Oster 1994; Qadir & Oster 2004; Rhoades et al. 1999). Each management option is specific to the soil and its condition and needs to be carefully addressed to be able to ensure strategic use of the MQSS water (Bennett et al. Submitted; Bennett & Raine 2012; Rengasamy et al. 2015). The lower the SAR, the less likely the water is to cause structural degradation of susceptible soils. Table 2.1 outlines the levels at which SAR indicates a hazard to soil structure DAFF (2012).

Table 2.1. Hazard levels for sodium adsorption ratio (DAFF 2012)

SAR_w	Hazard
<10	Safe to irrigate with no structural deterioration but salt-sensitive plants many be affected depending on EC/TDS
10-18	Hazard on fine textured soils with a high cation exchange capacity. Suitable on course textured soils with good drainage
18-26	Hazard on most soils. Need to manage with amendments and drainage (i.e. leaching)
26	Not suitable for irrigation

However, these hazard levels are not universally correct, but do provide a useful starting point upon which managers might seek to vary from. Where a variation of management is sought against hazard and ANZECC guidelines, then careful investigation of soil tolerance to SAR and EC must occur within the context of cropping salinity tolerances. In essence, if the water is to be used beyond the lower threshold of the ANZECC guidelines then there is need to understand the soil-specific response.

2.2.4 Reliance on poor quality water

While this thesis principally discusses the use of MQSS water as an optional resource, there are circumstances where there is no alternate option, which justifies the importance of understanding the mechanisms and dynamics of its use. Generally, farmers cannot control the quantity or quality of water they receive, which is a common problem with small-scale farmers in developing countries who have no other option than to use diluted or untreated wastewater. Farmers unquestionably prefer to irrigate with non-saline-sodic water, but globally there are many areas where only saline or sodic water is available. For example, in India an estimated 32 billion of the

135 billion cubic meters of groundwater withdrawn annually is saline (Qadir et al. 2007b), while Egypt plans to increase the reuse of marginal quality water from 10% to 17% by 2017 (Central Water Commission 1988; Qadir et al. 2007b).

Another reason for its use in developed countries are the environmental policies preventing farmers from being able to discharge the drainage water into rivers or lakes, leaving reuse as the only economically viable option (Bahri 2009). In the United States, municipal water reuse accounted for 1.5% of water withdrawals in 2000, with Californian residents reusing 0.656 ML of municipal wastewater annually (Molden 2007). In Australia, recycled water represents 2% of the total water consumption estimated to be at around 425 GL (Shanahan & Boland 2008). However, 66% of the total recycled water or 280 GL, was used by the agriculture industry in 2004–05. The highest use of recycled water was by the grains industry (118 GL or 42%) followed by the dairy (79 GL or 28%) and pasture (40 GL or 14%) industries (Shanahan & Boland 2008). Much of this recycled water would fit the definition of MQSS water at the discharge point following industry use. Thus, it is important to recognise treatment requirements prior to land application. For the coal seam gas (CSG) industry, the produced water is a by-product with salinity=2–12 dS/m and SAR=56–124 (Bennett et al. 2016b; Kinnon et al. 2010), which is well in excess of amounts that should be applied to soil. The treatment expense depends on the target EC and SAR, but increases exponentially as the SAR target becomes closer to 0 (Bennett & Raine 2017). Therefore, determining treatment based on soil-specific response has economic merit irrespective of CSG or agricultural industries.

2.3 Factors controlling soil structural stability

Soil structure is a crucial property to the function of several properties important to soil productive capacity, environmental quality and agricultural sustainability (Lal 1991), and is defined as:

> *"the size, shape and arrangement of solids and voids, continuity of pores and voids, their capacity to retain and transmit fluids and organic and inorganic substances, and ability to support vigorous root growth and development" (p 169).*

In order to critically discuss the soil structural dynamics in terms of MQSS water application, it is first important to briefly present the various factors affecting soil structure and how these operate. The stability of effective pores depends on the

stability of soil aggregates and the strength of bonds between soil structural units, with various factors controlling these bonds (Table 2.2). A more detailed explanation of the fundamental factors is presented in Appendix 10.1.

Table 2.2. Impact of soil properties and the mechanism on soil structural stability (Rengasamy et al. 2015)

Soil factors	*Mechanism*
Clay mineralogy and clay content	Charge originates in clay structures because of isomorphic substitution 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.
Soil pH	Alters the charge on broken bonds by adsorption of H^+ or OH^- ions; as pH increases, negative charge on soil particles increases.
Organic matter	Organic molecules bonded to clays by covalent bonding reduce the hydration charge of clay particles. Unbound organic molecules can increase the hydration charge. Hydrophobic organic matter can eliminate water interaction.
Inner sphere complexes	Cations such as iron (Fe), aluminium (Al), K fixed by clay minerals by inner sphere complexation reduces the hydration charge.
Cementation	Cementation of soil particles by Fe and Al oxides or calcium carbonate can block the charge available for water interaction.
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.
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.

2.4 Soil response to saline-sodic water

It has been established that soils respond specifically to a given water quality. The C_{TH} represents the point where a somewhat arbitrary reduction in soil hydraulic conductivity has occurred for a set SAR value, at a given EC without catastrophic decline in soil structure. This section expands on the concept of C_{TH} as it applies to fundamentals of swelling and disaggregation, and identifies knowledge gaps associated with current methodologies for determining C_{TH}.

2.4.1 Swelling and disaggregation

There are two types of swelling that can occur within a soil: 1) crystalline and 2) osmotic (Karpiński & Szkodo 2015). Crystalline swelling (sometimes called surface hydration) occurs when the clays are exposed to concentrated brine or aqueous solutions containing large quantities of divalent or multivalent cations (Karpiński & Szkodo 2015). Osmotic swelling occurs when the concentration of cations between the

layers is greater than that in the bulk solution (Norrish 1954). Water is osmotically drawn between the unit layers and the d-spacing (interlayer spacing) is increased where the concentration of cations between unit layers in a clay mineral is higher than that in the surrounding water (Patel et al. 2002). Osmotic swelling results in larger overall volume than surface hydration, however, only a few clays, like Na-montmorillonite swell in this manner (Norrish 1954).

There are two types of layer spacing: the intercrystalline is what occurs between the clay domains within the clay platelets, while intracrystalline is the space between the clay lattices (Slade et al. 1991). Previously when the term swelling was used it referred to both forms of spacing. Intercrystalline swelling, – as shown in bottom half of Figure 2.3- results from an increase in repulsive pressure and a decrease in attractive pressure due to a change in the diffuse double layer (Quirk 2001; Quirk 1994) and can be defined as disaggregation (Bennett et al. Submitted). This helps explain certain soil physical conditions, for example why kaolinite and illite are able to hold more water under disaggregation conditions as opposed to absolute stability (Figure 2.3).

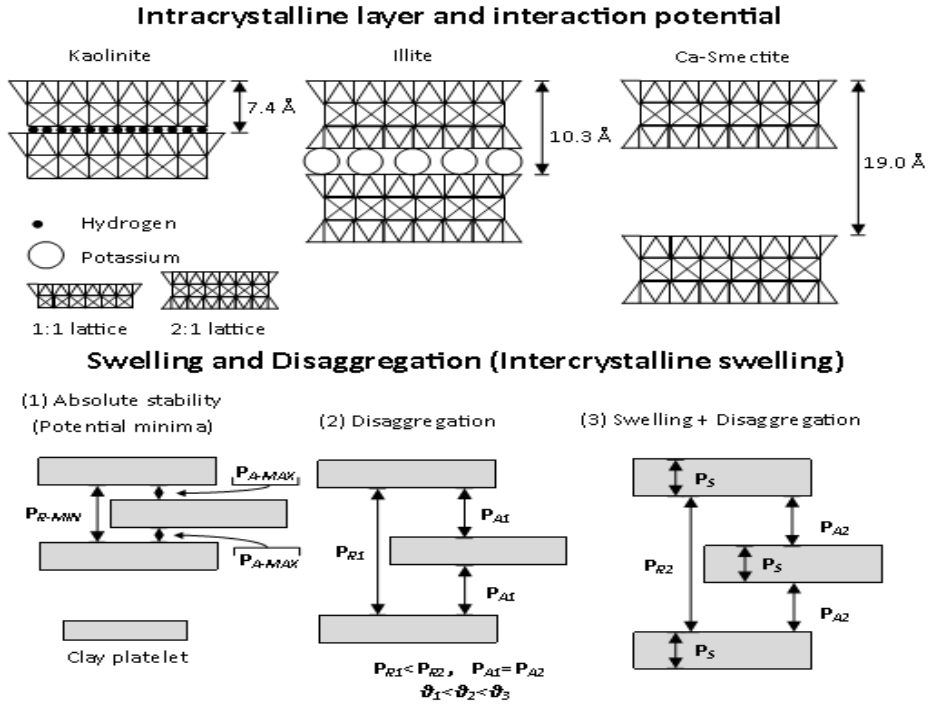

Figure 2.3. Difference between intercrystalline and intracrystalline swelling. This figure also shows how the difference leads to the conclusion of creating a distinction between swelling and disaggregation (Bennett et al. Submitted). P_R is the repulsive pressure equivalent to the diffuse double layer, and P_A are the attractive pressures principally governed by London van der Waals forces

2.4.1 Threshold electrolyte concentration

The concept of threshold concentration was introduced by Quirk and Schofield (1955) in their landmark paper on the effect of electrolyte concentration on soil permeability in relation to sodicity. Quirk and Schofield (1955) defined C_{TH} as the concentration of salts required to maintain a 10% decrease in soil permeability for a given soil ESP and SAR of the percolating solution. The key finding from this experiment was that permeability of the Na-saturated clay was maintained provided the electrolyte concentration was sufficiently large. The C_{TH} varied from soil to soil and even within the soils of similar clay content and type (Rhoades et al. 1999).

Various researchers have developed soil stability indicators for different soils in relation to the total salinity concentration and SAR of the water applied (Bennett et al. 2016a; Rengasamy & Marchuk 2011; Rengasamy & Olsson 1991; US Salinity Laboratory Staff 1954). Since soil hydraulic conductivity and infiltration is affected by soil type, clay mineralogy, clay content, and organic matter and more, C_{TH} is not a function of just SAR and EC, but of soil properties as well. These functions however, can be altered by the negative charge density on the soil particles. The negative charge is determined by the nature of clay minerals in a soil, dynamic changes in soil organic matter, aggregate and particle sizes and soil pH (Chorom et al. 1994; Rengasamy et al. 2016). Soil management practices affect the way in which these negatively charged sites are chemically bound and the proportion of these sites available for Na and water interactions (Chorom et al. 1994; Rengasamy et al. 2016). The following sections seek to investigate C_{TH} mechanisms and those that potentially define the soil-specific response.

2.4.1.1 *Threshold electrolyte concentration as an arbitrary value*

The C_{TH} is generally understood to represent the electrolyte concentration (directly proportional to electrical conductivity) at which a soil will remain stable when subjected to a given SAR solution, without limiting dispersion (McNeal & Coleman 1966; Quirk & Schofield 1955). Using this approach, Ezlit et al. (2013) modified the model of McNeal and Coleman (1966), explaining C_{TH} as the boundary between soil complete aggregation (potential minima observed within a pure Ca solution) and disaggregation (swelling and dispersion). This infers the point is arbitrary, as swelling occurs on a continuum up to the point that spontaneous dispersion occurs. This led numerous authors (e.g. Rengasamy et al. 2016) to suggest that the critical threshold

occurred at the point of spontaneous dispersion, or the aggregate-dispersion boundary (C_{TU}). It is noted that C_{TH} represented a smaller reduction in hydraulic conductivity than has been observed for the C_{TU} (Bennett & Raine 2012; McNeal & Coleman 1966), meaning that the C_{TH} occurs at a lower EC than the C_{TU} for the same SAR (Quirk 2001).

As discussed, the threshold electrolyte concentration is generally regarded as an arbitrary value because the hydraulic conductivity gradually decreases as sodicity increases and there is not a single point reduction that can be considered the true C_{TH} (Quirk & Schofield 1955). That is, the C_{TH} is effectively a measureable departure form the potential minima taking into account the extent of measurement error. It differs from the aggregation-dispersion boundary in that it is defined as a 10% reduction in K_{sat} from the potential minima and that the clay domains are still intact. As the aggregation-dispersion boundary is approached smaller domains may disperse while larger ones remain intact, although as the boundary is breached it is expected that all domains become inherently unstable. Table 2.3 details the various rK_{sat} associated with the C_{TH} appearing in the literature. The fact that these differ is due to the C_{TH}- not existing at a defined point, but as a measureable departure from absolute stability. For the purpose of this thesis rK_{sat}=20% is used as it better allows for measurement error in leaching experiments, is apparently practically relevant in terms of protecting soil aggregates from complete spontaneous dispersion (Ezlit et al. 2013) and is essentially the average of reported values.

Depending on the soil, the practically acceptable reduction in K_{sat} might be much greater than 10% — for example a sandy soil with high initial K_{sat} — and management guideline limits could be expanded to allow greater reduction, provided the true conductivity of the soil is considered (de Menezes et al. 2014).

Table 2.3. Variation in the reported threshold electrolyte concentration

Critical reduction point	Source
10%	Quirk and Schofield (1955)
25%	McNeal and Coleman (1966)
20%	Cook and Muller (1997); Quirk (2001)
15%	Quirk (2001)
20%	Bennett and Raine (2012)

In the case of de Menezes et al. (2014) a reduction of 20% was used in accordance with Bennett and Raine (2012) for two soils and the applicability of a percent reduction threshold was discussed in terms of initial hydraulic conductivity; i.e. a 20% reduction in a very low initial hydraulic conductivity value is still a very low value and vice versa, which is likely to affect practical irrigation feasibility. This work discussed the use of minimum conductivity guideline, but did not investigate this further. Therefore, in the formulation of new management guidelines, this should remain a consideration.

2.4.1.2 *Soil Specific response*

Substantial differences in C_{TH} curve dimensions have been identified between different soil types, due to variations in mineralogy (Churchman et al. 1993), clay content (Frenkel et al. 1978; Goldberg et al. 1991; McNeal & Coleman 1966) and organic matter type and content (Nelson & Oades 1998). However, no direct relationship has been established between these properties and C_{TH} curves (Bennett & Raine 2012). In fact, even similar soil types may show very different C_{TH} curve relationships (Figure 2.4) (Bennett et al. Submitted) consequently making it difficult to predict a C_{TH} curve for any given soil.

Bennett and Raine (2012) and Bennett et al. (Submitted) showed that there were significant differences between soil C_{TH} curves for soils, even within the same soil order. Further, the C_{TH} solution concentration using a 20% reduction in hydraulic conductivity was soil and site specific. Bennett et al. (Submitted) undertook C_{TH} analysis on 58 soils and depicted it by soil type (Figure 2.4). The soil orders and C_{TH} did not demonstrate a clear relationship, demonstrating a soil-specific response again, which confirms the findings of (McNeal & Coleman 1966) for their limited data set. Bennett and Warren (2015), while examining the reduction in soil saturated hydraulic conductivity due to effluent application, demonstrated the practical significance for two soil sites with highly contrasting soil-specific response. For one soil the conductivity was observed as reducing, but for the other soil, under the exact same solution cation suite and concentration, the conductivity was observed to be improving. Importantly, the engineering guidelines for effluent pond preparation, that the work was conducted for, assumed that such solution quality would decrease the hydraulic conductivity dramatically, which was clearly not so and would have had environmental ramifications beyond the design specification. This clearly establishes that there is need to better understand the mechanisms controlling the soil-specific

response in order to be able to predict such occurrence given a set of soil and solution attributes.

2.4.1.2.1 Factors impacting soil-specific response

Research still needs to be undertaken to find a clear quantified understanding of the soil-specific response controlling mechanisms for C_{TH}. The factors generally attributed to the variations are mineralogy (Churchman et al. 1993), clay content (Frenkel et al. 1978; Goldberg et al. 1991; McNeal & Coleman 1966) and organic matter type and content (Nelson & Oades 1998), which has previously been presented in this review. In relation to this, Bennett et al. (Submitted) analysed 30 different soils and found no direct correlation between the C_{TH} and organic matter, soil clay content, cation exchange capacity, the clay cation ratio, pH, or the clay mineral suite. Only clay content was shown to have any direct effect on the soil-specific occurrence of the C_{TH}. The type and amount of clay mineral in soil is thought to be the dominating factor relating to soil dispersion/flocculation and reduction in hydraulic conductivity (Ezlit et al. 2013; Goldberg et al. 1991). The influence of clay mineralogy and clay content on C_{TH} is not clearly understood. Soil clay mineralogy can significantly affect a number of soil physical and chemical properties (Marchuk et al. 2013a). It has been well established, usually in a semi-quantitative or qualitative sense, that effects of exchangeable cations and electrolytes on swelling and dispersion of soil aggregates are largely dependent on the dominant type of clay mineral present in the soil (Churchman et al. 1993). This should explain why Bennett et al. (Submitted) clearly showed that semi-quantitative analysis of clay mineralogy had a consistent trend of explaining variation within the data set, although not significant, and suggested that quantifiable mineralogical analysis would lead to a better mechanistic understanding.

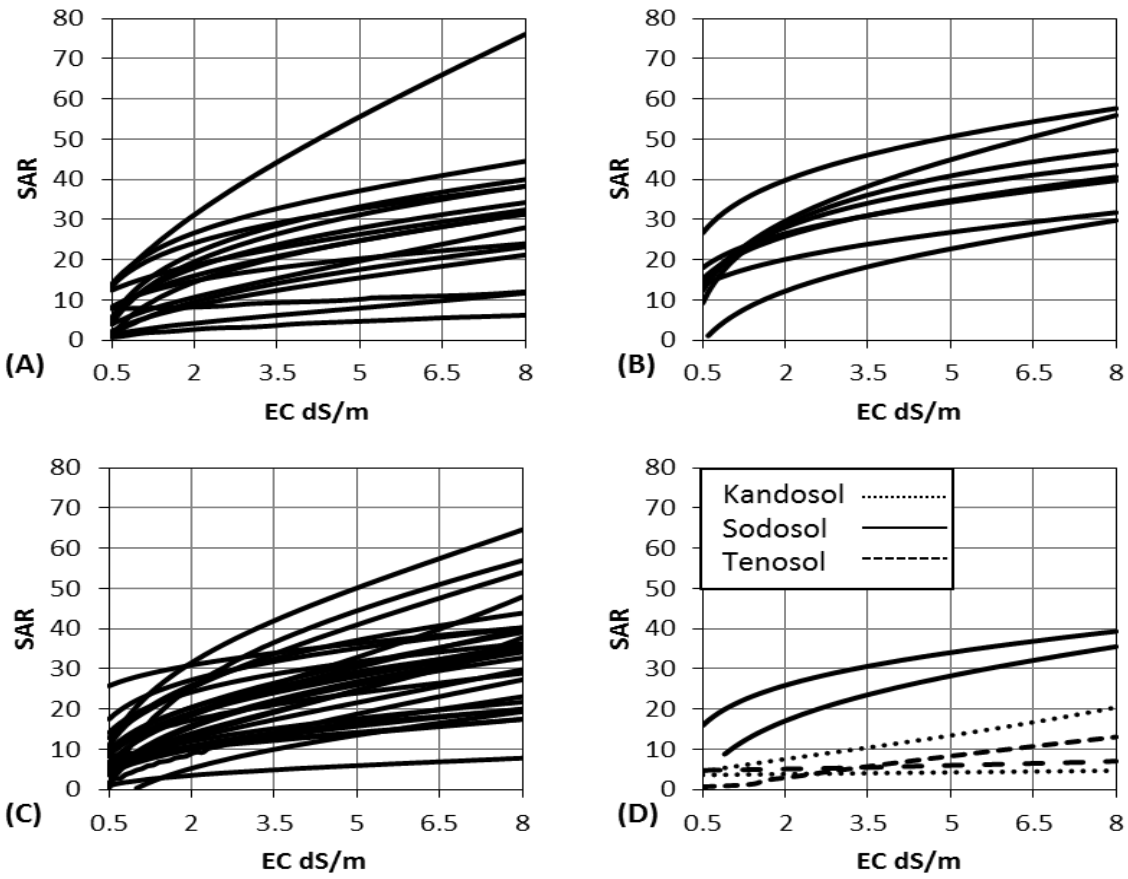

Figure 2.4. Threshold electrolyte concentration curves observed for (A) 14 Chromosols; (B) 8 Dermosols; (C) 30 Vertosols; and (D) two soils per three other soil orders. Threshold electrolyte concentration was defined as a 20% reduction in saturated hydraulic conductivity, as per Ezlit et al. (2013). Source: Bennett et al. (Submitted).

Another mechanism that is thought to be a controlling mechanism behind the soil specific response of C_{TH} is the clay platelet charge density. The pressures that determine the stability of the clay domain, slit-shaped pore model, are a function of the charge density, which is controlled by the clay mineralogy and clay crystal physical dimensions. Quirk (2001) showed that the charge density present at the boundary between the stern layer and DDL is most likely the cause of the swelling pressure at the domain. It is likely that the soil-specific response of C_{TH} can be partly attributed to the variation in the charge density of clay minerals with clay type, the size of the crystal overlap, and the size of the slit-shaped pore. This is also related to net negative charge approaches of Marchuk et al. (2013a). The domain concept of Quirk (2001) is largely accepted, but does not currently incorporate the ionicity approaches of Marchuk and Rengasamy (2011) who show that clay dispersive behaviour is related to the ionicity of clay-cation bonds and the extent of covalent bonds in particular; these being

stronger than short range van der Waals forces. Thus, expanding the domain concept to include recent ionicity approaches would have merit.

Quirk (1994) mentioned that organic matter, which can stabilise soil aggregates against slaking, can also induce clay dispersion. Tisdall and Oades (1982) explained the importance of organic matter to the stability of soil aggregates from macro through micro levels in terms of soil aggregates sizes. However, Bennett (Submitted) found that organic matter explained less than 3% of data variance in C_{TH}. They did not dispute the importance of organic matter to aggregate stability as explained by Tisdall and Oades (1982), but instead suggested that the strength of these organic bonds was not sufficient to overcome the swelling and disaggregation pressures occurring within the clay domain. Hence, they hypothesised that organic matter did not become important in controlling aggregate stability in terms of dispersion until the system approached the aggregation-dispersion boundary. This suggests that there is no evidence for a direct relationship between C_{TH} and organic matter, but that this would require further investigation to accept such an alternative hypothesis.

2.4.1.3 ***Turbidity Concentration***

Quirk and Schofield (1955) developed a significant distinction between initial hydraulic reduction and spontaneous dispersion defining these as different concentration thresholds; the C_{TH} and threshold turbidity concentration (C_{TU}), respectively. The C_{TH} describes the first apparent effect on soil structure, while the C_{TU} refers to the point at which the concentration of the solution is at about a quarter of the threshold concentration and dispersed clay particles start to appear in the percolating solution (Quirk 2001). At this point, the dispersed particles start appearing within the percolate causing a dismantling of the soil microstructure. Such a model might suggest that hydraulic conductivity reduction between the absolute stability and immediately prior to the C_{TU} is a completely reversible process. However, one must consider that in hydraulic conductivity experimentation used to determine the threshold values that bulk properties are being measured. That is, clay domains will occur at different magnitudes of particle sizes and these would logically have differing threshold concentrations based on the clay domain charge density and ionicity concepts. So, the process should be considered partially reversible. This is something that requires further investigation (McNeal 1968).

Before Quirk (2001), confusion existed with regards to the definition of the term 'threshold electrolyte concentration' as it was assumed to be the "electrolyte concentration required to flocculate a dispersed suspension of the soil. It is an important distinction that flocculation and dispersion processes are two distinctly different processes and that flocculation has no real role in transitioning from an aggregated state to a dispersed one; i.e. flocculation is a property of a dispersed suspension of clay in water (Quirk 2001). Wearing (2005) indicated that the smaller turbidity concentration is because the particles have to be removed from a potential well where the clay crystals overlap.

The threshold concentration (C_{TH}, mmol(+)/L), with respect to SAR, has been calculated by the following equation (Quirk 1971, 2001):

$$C_{TH} = 0.56SAR + 0.6 \quad (SAR\ 0-32) \qquad \text{Equation 2.1}$$

The turbidity concentration (C_{TU}) has been given by (Quirk 2001; Quirk et al. 1986):

$$C_{TU} = 0.16SAR + 0.2 \quad (SAR\ 0-32) \qquad \text{Equation 2.2}$$

It should be noted that these functions are not universal, but descriptive as an average function for a range of soils used in the various works of Quirk. The turbidity concentration is many times smaller than that required to flocculate a dispersed suspension of the soil (Quirk 2001) and is associated with spontaneous dispersion (Figure 2.5), defined by Quirk (2001) as the point where dispersed clay was first observed in the leachate. Quirk and Schofield (1955) found that the turbidity in the percolate increased with increasing SAR values. Rengasamy et al. (1984) gave the equation TCC=1.21SAR+3.3 for spontaneous dispersion for a collection of red-brown earth soils that had been subjected to end-over-end shaking. Quirk (2001) reported that though the two turbidity concentration equations are very similar, the differences are the result of the mechanical shaking of the clay domain structures. These being dismantled by the energy imparted to the soil during the shaking procedure. The C_{TU} therefore, occurs at the boundary of soil being in an aggregated state or a dispersed state. As described above, this will differ depending on the clay domain size under Brownian motion and equivalent solution conditions.

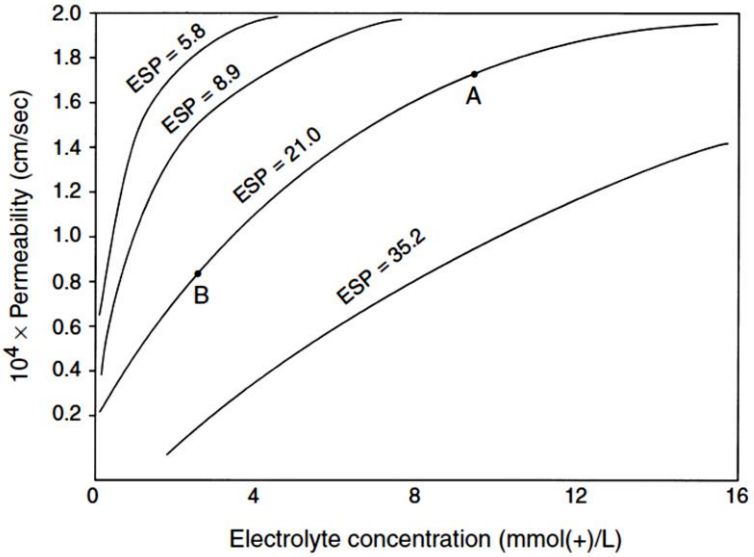

Figure 2.5. Difference between the threshold electrolyte concentration (A) and the turbidity concentration (B) in relation to the ESP and EC (Quirk 2001).

2.4.2 The importance of ionisation potential

2.4.2.1 *Covalency and the ionicity index*

The type of bonding between clay particles as mediated by the cations determines the water stability of an aggregate. Water molecules easily solvate the ionic bonding but there is no effect on covalent bonding (Rengasamy & Olsson 1991). The degree of covalency, or ionicity, in a bond involving a metal cation is characterised by the Misono softness parameter derived from their ionization and ionic potentials (Rengasamy & Sumner 1998). Dispersive behaviour of clays bonded by metallic cations can therefore be explained using the Misono softness parameter as a criterion.

Polarizability is employed as a basis to favour covalent bonding between a cation and an anion. Anions can be polarized to a greater effect with small sized, highly charged cations as compared to large-sized and/or monovalent cations (Huheey et al. 1993). This is defined by the ionic potential:

$$IP = Z/R \qquad \text{Equation 2.3}$$

where Z is the charge of the cation and R is its radius. Ionic potential indicates the strength and weakness of an ion's electrostatic attraction to ions of opposite charge, and the extent of repulsion of the like charged ions.

The ionicity index was developed in Marchuk and Rengasamy (2011) by using the covalency index derived through a combination of the ionic potential (Equation 2.3) and the Misono Softness parameter (Equation 2.4). The Misono's softness parameter is used to define the 'softness' or high polarizability of a cation. It is given through the following equation where R is the ionic radius of the cation with a valence Z and whose ionisation potential is I_z, and I_{z+1} is the ionisation potential when the valence of the cation changes to Z+1:

$$Y = (I_z R / Z^{0.5} I_{z+1}) \qquad \text{Equation 2.4}$$

Marchuk and Rengasamy (2011) made the assumption that the covalency or ionicity index of a cation alone will indicate the degree of covalent or ionic character of the clay–cation bonds. Therefore, they combined the ionic potential and the Misono Softness parameter to derive the covalency index and on the basis of that the iconicity index:

$$CI = (I_z / I_{z+1}) Z^{0.5} \qquad \text{Equation 2.5}$$

$$II = 1 - CI \qquad \text{Equation 2.6}$$

On that basis, Marchuk and Rengasamy (2011) used the ionisation potentials and Misono softness parameters presented in the Handbook of Chemistry and Physics (Weast et al. 1989), to calculate the Covalency index and the Ionicity index for the major cations in Table 2.4.

Table 2.4. Calculations of ionicity and covalency indices for Li+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} using ionisation potentials from the Handbook of Chemistry and Physics (Marchuk & Rengasamy 2011)

Cation	IP, ionic potential (nm^{-1})	Y Misono softness parameter (nm)	Covalency index (CI)	Ionicity Index (II)
Li^+	13.5	0.05	0.07	0.93
Na^+	9.8	0.11	0.11	0.89
K^+	7.2	0.19	0.14	0.86
Mg^{2+}	27.8	0.10	0.27	0.73
Ca^{2+}	20.2	0.16	0.33	0.67
Sr^{2+}	17.2	0.21	0.36	0.64
Ba^{2+}	17.6	0.23	0.40	0.60

2.4.2.2 ***Dispersive Potential***

In order to derive a single parameter that will combine the effects of several factors affecting clay dispersion, Rengasamy (2002) detailed the method of measuring '*dispersive potential*', which is derived from the electrolyte concentration and composition preventing the tendency of soil aggregates to disperse spontaneously (or mechanically). The dispersive potential indicates the energy associated with the dispersive reactions in soil–water interactions. The different effects of the cations are also taken into account in the calculation, as an integration rather than a discrete measure. The difference between osmotic pressure between the C_{TH} (P_{tec}) required to achieve a complete flocculation of the clay particles and the osmotic pressure at the given soil solution concentration (P_{sol}) is defined as the dispersive potential (P_{dis}) (Marchuk & Rengasamy 2012).

$$P_{dis} = P_{tec} - P_{sol} \qquad \text{Equation 2.7}$$

The osmotic pressure at the threshold point (P_{tec}) can be calculated by multiplying the concentrations of Ca, Mg, K and Na (mmol/L) within the equilibrium solution, by each cation's flocculating powers, Ca=45, Mg=27, K=1.8, and Na=1 (Rengasamy & Sumner 1998).

$$P_{tec} = 3.6 \times \left(45 \times C_{Ca} + 27 \times C_{mg} + 1.8 \times C_K + C_{Na}\right) \qquad \text{Equation 2.8}$$

Dispersive potential was designed to be a uniting concept that rapidly provides information on a soil-specific basis via the tendency for a clay particle to disperse. Marchuk and Rengasamy (2012) concluded that dispersive potential of clay might be more useful for management of soils. However, there are a few concerns present. Theoretically, it is crucial to remember that dispersive potential actually calculates the turbidity concentration (C_{TU}) (Quirk & Schofield 1955). The C_{TU} refers to the point at which dispersed clay particles start to appear in the percolating solution and the concentration of the solution is at about ¼ of the C_{TH} for the soil investigated in Quirk and Schofield (1955) and presented in Quirk (2001). There would be merit in relating the P_{dis} to both the C_{TH} and C_{TU} to further explore the two approaches.

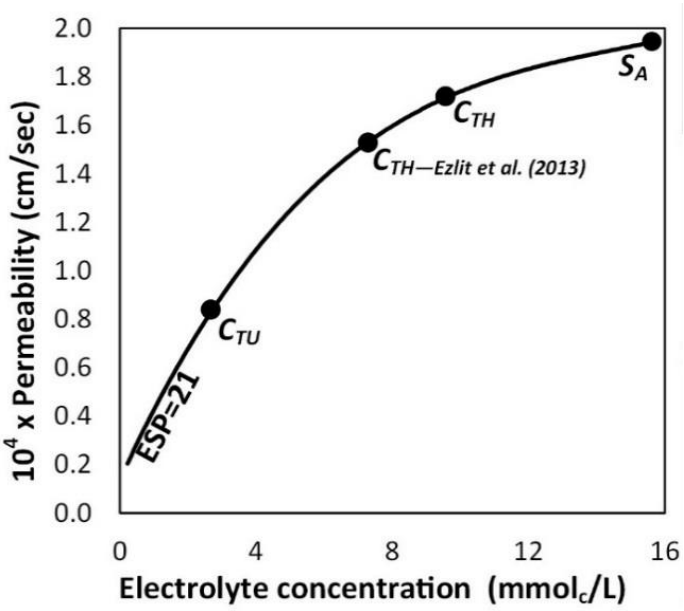

Figure 2.6. Hydraulic reduction curve at ESP 21 with the turbidity concentration (C_{TU}) and threshold electrolyte concentration as defined by Quirk and Schofield (1955) (C_{TH}; 10% reduction in permeability) identified, along with the absolute stability (SA) and C_{TH} as defined by Ezlit et al. (2013) (20% reduction in permeability).

Currently, the P_{dis} is a method that has only been tested on soils that are already dispersive or soils that have dispersed through the use of simulated rainfall (Marchuk & Rengasamy 2012; Rengasamy 2002). The practicality of the method to determine an irrigation water quality suitability to a non-dispersive soil has not been tested in equilibration with the irrigation solution.

2.4.2.3 *Net Dispersive charge*

Rengasamy et al. (2016) introduced the concept of the net dispersive charge (NDC), which is a representation of the charge available for water interaction. The NDC is based on the exchangeable cations at a given soil pH and the concentration of soluble cations in the dispersed suspension, and is the difference between the dispersive charge and the flocculating charge in mmol$_c$/L:

$$\begin{aligned} &\text{net dispersive charge} = \text{dispersive charge} - \text{flocculating charge} \\ &\text{dispersive charge} = [\text{Ca}] + 1.7[\text{Mg}] + 25[\text{K}] + 45[\text{Na}] \\ &\text{flocculating charge} = 45[\text{Ca}] + 27[\text{Mg}] + 1.8[\text{K}] + [\text{Na}] \end{aligned} \qquad \text{Equation 2.9}$$

The dispersive and flocculating charges are derived with weighted factors allotted to individual cations and the coefficients for the cations in the dispersive charge are those of the flocculation charge but in reverse. If the net dispersive charge value is >0, the system will contain dispersed clay. Rengasamy et al. (2016) state that when the net

dispersive charge is equal to zero, the point of C_{TH} occurs. However, Quirk (2001) showed that the point of spontaneous dispersion (zero net charge) was equivalent to the turbidity concentration. Bennett et al. (Submitted) supports Quirk (2001) in suggesting that the zero net dispersive charge is a representation of the C_{TU}. It is important to note that the zero net dispersive charge is different to the point of zero net charge at which point the system contains no charge with which to interact with water molecules and is therefore stable.

2.5 Potassium and magnesium in relation to soil stability

The physical and chemical properties of a soil are greatly influenced by the cation suite present in the soil/water matrix. While traditionally the focus of dispersion has been placed on Na, and the focus of flocculation on Ca, however, both K and Mg have been considered to affect soil stability. Therefore, this section presents the new indices incorporating K and Mg, as well as briefly discussing their development. Additionally, their formulation theory is used to discuss the relevance of a universal approach, and the potential for soil characteristics to demand a specific response, given what is known about ionisation potential and clay mineral characteristics.

2.5.1 Indices incorporating for the presence potassium and magnesium to describe soil-water relations

2.5.1.1 *SAR and PAR*

Most research around saline-sodic waters focuses on Na cation (Rengasamy & Olsson 1991) because Na salts are all very soluble and therefore, found in all natural waters. The presence of Na in irrigation water or the soils has always been a serious concern because its excessive presence in soil can have a detrimental effect on the physical properties required for plant growth (Evangelou & McDonald Jr 1994). The SAR is used to predict the potential for Na to accumulate in the soil, if sodic water was in constant use (Rengasamy & Churchman 1999). This parameter qualifies the ratio of Na to Ca and Mg in terms of the ability of the Na to dominate the soil. SAR is an index therefore is without dimensions.

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \qquad \text{Equation 2.10}$$

Due to both Ca and Mg being divalent ions, it was assumed that they both would have equivalent effects on the soil structure. However, there is a difference between the Ca and Mg ionicity, meaning Ca has a greater abundance of covalent bonds as compared to Mg, and thus is more efficient in maintenance of soil stability (Bennett et al. 2016a; Smith et al. 2015). This has an effect on the extent of the hydration and therefore, there is a difference in the swelling and dispersion processes. Calcium and Mg will generally keep soil flocculated because they compete for the same spaces as Na to bind to clay particles (Dontsova & Norton 1999; Warrence et al. 2002). Increased amounts of Ca and Mg can reduce the amount of Na-induced dispersion. However, SAR also does not take into account the effect of K, nor the differing effect of Ca and Mg.

Potassium can cause a decrease in the permeability of a soil similar to Na (Quirk & Schofield 1955), due to both being monovalent cations. The effect of K on soil structural stability has been debated to be either equal or less than the effect of Na (Chen et al. 1983; Robbins 1984; Smiles & Smith 2004). Based on the large hydrated ion size and its affinity for clay minerals, high levels of exchangeable K in soil have the potential to cause clay swelling and dispersion (Levy & Feigenbaum 1996). Potassium adsorption ratio (PAR) defined by the concentrations of K^+ and Ca^{2+} and Mg^2 is less widely adopted than the SAR. Furthermore, it ascribes an equivalent effect of K as compared to Na, and does not account for differing effects in terms of Ca and Mg either.

$$PAR = \frac{K^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \qquad \text{Equation 2.11}$$

2.5.1.2 *Cation ratio of soil Structural Stability*

Smiles and Smith (2004) concluded that neglect of K, and the simple appeal of SAR to infer soil structural stability will be misleading and, to meet this need, suggested a 'monovalent cations adsorption ratio' (MCAR), which includes Na and K in the calculation of SAR. MCAR assumes that the flocculating effects of Ca^{2+} and Mg^{2+} are the same, and the dispersive effects of Na^+ and K^+ are the same.

$$MCAR\ (\frac{mmol}{l}) = \left(\left[\frac{[Na] + [K] + [NH]}{\left(([Ca] + [Mg]) \div 2\right)^{0.5}}\right]\right) \qquad \text{Equation 2.12}$$

However, MCAR does not take into account that Na and K also have different ionicity indices. This means that different dispersive powers of Na and K, and different flocculating power of Ca and Mg. Therefore, their effect on the soil is not equal (Rengasamy & Marchuk 2011; Robbins 1984).

Rengasamy and Sumner (1998) determined the flocculating powers of the prevalent cations: Na, K, Mg and Ca. On the basis of MCAR, but incorporating the different dispersive and flocculative effects, the cation ratio of soil stability (CROSS) was developed (Rengasamy & Marchuk 2011).

$$CROSS = \frac{Na + 0.56K}{\sqrt{\frac{Ca + 0.6Mg}{2}}} \qquad \text{Equation 2.13}$$

The CROSS was found to be superior to SAR (Figure 2.7) in predicting dispersion in soils that contain Na and K (Rengasamy & Marchuk 2011)

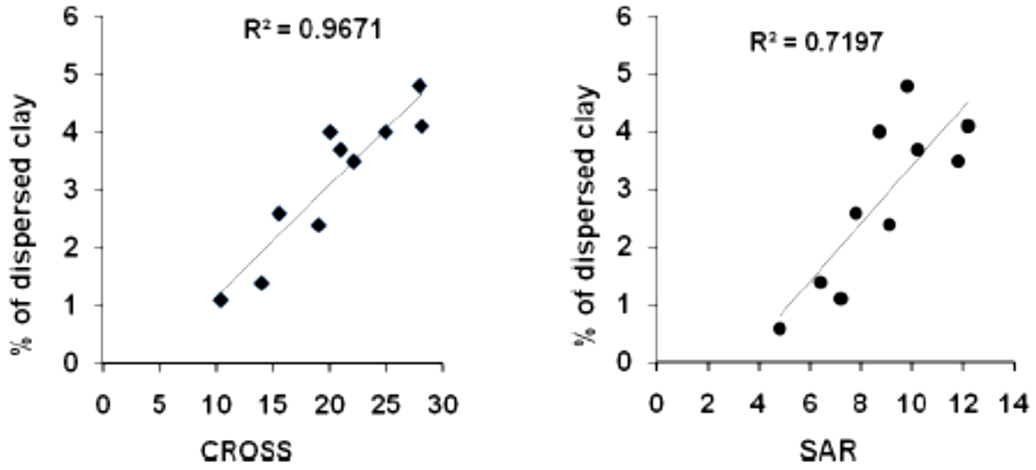

Figure 2.7 Correlations between % of dispersed clay with either SAR or CROSS using soils containing higher amounts of K than Na; and Mg than Ca (Marchuk & Rengasamy 2010).

Marchuk and Rengasamy (2012) concluded that C_{TH}-CROSS relations were specific to soil type and cannot be generalised because of several interacting mechanisms that control the soil structure including soil organic matter, clay contents and mineralogy and different attributes of the soil solution. Further, Marchuk and Rengasamy (2012) found that the net charge on clay surface measured as zeta potential largely appeared to explain soil specific variation in C_{TH}.

2.5.1.3 *Exchangeable dispersive potential as an alternate to exchangeable sodium potential*

A sodic soil in Australia is usually identified as one with an ESP (Equation 2.14) greater than 6%:

$$ESP\% = \left(\frac{(Na)}{[exch(Na + K + Ca + Mg)]}\right) \times 100 \qquad \text{Equation 2.14}$$

Rengasamy and Marchuk (2011) suggested the theory of exchangeable cation ratio (ECR) instead of ESP to determine the potential for a soil to disperse. This formula (Equation 2.15) involves a modification that takes into account the percentage of difference in the effect of Na to K when clay dispersion occurs, but suggested that Na and K should be additive and equivalent in effect.

$$ECR\% = \left(\frac{(Na + K)}{[exch(Na + K + Ca + Mg)]}\right) \times 100 \qquad \text{Equation 2.15}$$

The initial form of ECR did not account for the dispersive effects of exchangeable Mg, identifying a need for an equation that also explained soil dispersion with an inclusion of specific exchangeable cation effects. With the growing importance of dispersive coefficients in explaining clay colloidal behaviours in models such as CROSS, it is necessary to design an equation on that basis. Therefore, on the basis of the ionicity values derived by Rengasamy and Marchuk (2011), Bennett et al. (2016a) derived an equation that incorporates the dispersive effects of Mg known as the exchangeable dispersive potential (EDP). This equation (Equation 2.16) has been validated against two different soils datasets. The authors concluded the contribution of Mg to soil dispersion is low under majority of conditions and only contributes where Mg concentration is 60% effective (Bennett et al. 2016a). This suggests that Mg has a specific effect and that its main role in disaggregation processes is expansion of the DDL beyond that of a Ca system, resulting in hydraulic reduction, but not necessarily dispersion. Additionally, as the ionicity concept is something that pertains to the solid phase, they demonstrated that the use of coefficients equating the K and Mg effect on dispersion as relative to Na improved the correlation of the index with dispersed clay.

$$EDP\% = \left(\frac{(Na + 0.556[K] + 0.037[Mg])}{[CEC]}\right) \times 100 \qquad \text{Equation 2.16}$$

2.5.1.4 *Incorporation into the guidelines*

In Australia, K and Mg in soil can occur naturally or due to excessive concentration of cations in poor quality irrigation wastewater (Arienzo et al. 2009; Marchuk 2013). There is a need to reconsider current guidelines used for irrigation management, especially as the requirement to irrigate with saline-sodic water increases, and develop a new set of guidelines that incorporate the presence of K and Mg in the soil. The previous guidelines involve calculating the threshold point on the basis of SAR. However, if CROSS produces more accurate results for Australian soils, the question arises if the guidelines need to be changed to incorporate CROSS. Similarly, EDP should be utilised within guidelines over that of ESP. Any changes to guidelines also need to consider soil specificity in terms of C_{TH} and the applicable water quality acceptable for a given soil.

2.5.2 Optimising coefficients of equivalence

In the development of both CROSS (Rengasamy & Marchuk 2011) and EDP (Bennett et al. 2016) cation flocculating powers were defined as:

$$\text{Flocculating power} = 100(I_z/I_{z+1})^2 Z^3 \qquad \text{Equation 2.17}$$

where Z is the valence of the cation, the ionisation potential of which is I_z, and I_{z+1} is the ionisation potential when the valence of the cation changes to Z+1. Based on this equation, the flocculating power of Na is assumed to be equal to 1 and that of K, Mg and Ca relative to this at K=1.8, Mg=27 and Ca=45 (Rengasamy 2002).

Smith et al. (2015) and Bennett et al. (2016a) suggested that the coefficients used in flocculating power could be optimised on a soil-specific basis. The initial data in Rengasamy (2002) varied substantially between soils, when considering the extent of the possible physical domain the values pertain to. Rengasamy (2002) used a mean value as a result, which improved the fit of data in general to dispersive extent of a given clay at a given solution, although Smith et al. (2015) demonstrated this could be improved further using a computational optimisation approach. This provides the necessary proof that the flocculating power associated with cations is also soil-specific. Smith et al. (2015) further used the C_{TH} values reported by Quirk (2001) to calculate

the coefficients for K and Mg on a dispersive, rather than flocculative, basis. Their reasoning was that the electrolyte concentration require to flocculate is much greater than that required for dispersion. When looking at dispersion instead of flocculation, coefficients of K was found to be 0.26 and for Mg analysis of the bivalent cations led to a coefficient of 0.3. Therefore, in terms of dispersion the new form of CROSS according to Smith et al. (2015) is:

$$CROSS_d = \frac{Na + 0.26K}{\sqrt{\frac{Ca + 0.30Mg}{2}}} \qquad \text{Equation 2.18}$$

Subsequently, they tested $CROSS_d$, CROSS and MCAR against the C_{TH} values from Quirk (2001). The results showed a good correlation between CROSS and C_{TH}; however a much stronger correlation was evident between $CROSS_d$ and C_{TH}. These results confirm that approaching the system from a dispersion basis is more appropriate than that of a flocculative basis.

Even though the generalised coefficients in Equation 2.18 provided a better fit than CROSS, the computational optimisation approach was better yet again. By comparison of CROSS with the definitions of SAR and PAR, Smith et al. (2015) were able to conclude that CROSS can be interpreted as a weighted sum of a generalised SAR and PAR. In this the weighting factor serving as a measure of the efficacy of PAR, relative to that of SAR, as a control on the soil property with which they are correlated. An optimization technique was used to obtain the best-fit values for *a* and *b* (where a and b are coefficients for K and Mg, respectively) based on soil C_{TH} and cation data. The resulting values of *a* and *b* were 0.335 and 0.0758, respectively, for their data. Therefore, they present Equation 2.19 in which the coefficients are presented as optimisable, rather than constants:

$$CROSS = \frac{Na + aK}{\sqrt{\frac{Ca + bMg}{2}}} \qquad \text{Equation 2.19}$$

Using a similar approach, Bennett et al. (2016a) suggested EDP was better presented as:

$$EDP\% = \left(\frac{(Na + \mathrm{a}[K] + \mathrm{c}[Mg])}{[CEC]}\right) \times 100 \qquad \text{Equation 2.20}$$

Where *a* and *c* are optimisable dispersive coefficients that create an equivalent effect for Mg and K based of Na.

Where *a* is the same coefficient as for $CROSS_d$, but *c* is determined as Mg dispersive extent equivalent to Na. The importance being that for both Equation 2.19 and Equation 2.20 that better explanation of dispersion on the basis of cations will be obtained where *a*, *b*, and *c* are optimised on a soil-specific basis. There is evidently need to better understand the variation in coefficients with soil type in order to move towards a predictive model for C_{TH} as these control the extent of ionicity.

Bennett et al. (2016a) raised an interesting result where Mg was determined to improve prediction under some circumstances, but make prediction worse under others. The issue of concern is that the specific influence Mg has on dispersion and that literature evidence for this further confirms a variable result. There are numerous definitions for a magnesic soil, usually on the basis of the Ca:Mg ratio. Isbell (2002) stated that a soil will be magnesic and dispersive if the Ca:Mg ratio is <0.1, while Rengasamy et al. (1986) suggest it is where Ca:Mg ratio is <1.0. On the other hand, He et al. (2013) found that the Ca:Mg ratio had no significant effect on the dispersion and soil structure except in pure Mg systems. Subsequently, Bennett et al. (2016a) determined that the Ca/Mg ratio (*r*) is redundant as a single measure and the effect of Mg is a function of the concentration the other cations in solution. They demonstrated that the *c*[Mg] term in Equation 2.20 should only be used where it was considered >40% effective, with effectiveness a function of *r* and C_{ex} (the sum of cation concentration other than Mg or Ca; Ca being accounted for in *r*), as depicted in Figure 2.8 However, this was mathematically determined and requires further investigation, although the coefficient is still suggested as optimisable.

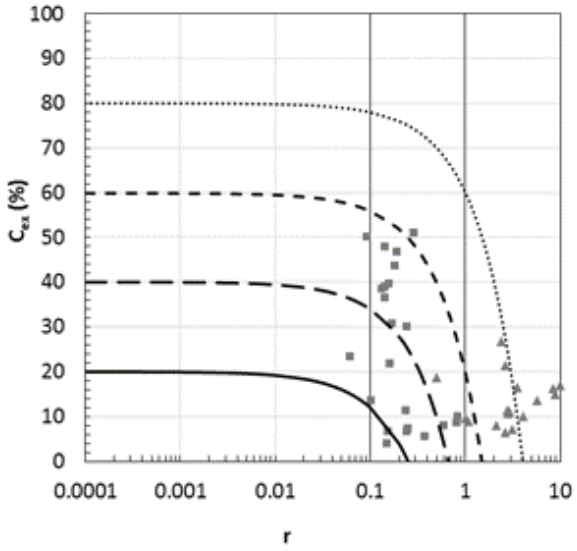

Figure 2.8 Australian (D) and Tanzanian (&) datasets showing 80% (—), 60% (– –), 40% (–) and 20% (···) reduction in magnesium effect contours; bold vertical lines at r = 0.1 and r = 1.0 represent Ca/Mg ratio threshold criteria as proposed in Isbell (2002) and Rengasamy et al. (1986). (Bennett et al. 2016a).

2.6 Towards predicting threshold electrolyte concertation

This section builds on the literature to identify opportunities to move towards prediction of the C_{TH} on a soil specific basis. The disaggregation model (Ezlit et al. 2013) is presented in some detail as it forms the basis of the thesis investigations. Limitations to current modelling predictive approaches are briefly discussed, and knowledge gaps that require further exploration are presented.

2.6.1 Limitations of current predictive approaches

There are limitations of the models that can handle water and solute movement associated with soil chemical reactions under sodic conditions (Murtaza et al. 2006). Simulation of soil-water flow and chemical processes under highly sodic conditions requires a consideration of the effect of soil structural degradation on water and solute transport under variable water content conditions. Modelling of unsaturated water and solute flow coupled with equilibrium ion chemistry has been carried out by a number of researchers (Jacques et al. 2008) .

SALF was designed as an equation that predicts the leaching faction (steady state drainage) under different irrigation, rainfall conditions and varying soil properties (Shaw & Thorburn 1985). This model works on the assumptions that soil hydraulic conductivity and soil leaching are connected, and soil hydraulic conductivity is

influenced by the clay content, clay mineralogy, and ESP (Shaw & Thorburn 1985). SALF is useful, but it does not provide the level of variability observed in C_{TH} for the soils in Bennett et al. (Submitted).

Hydrus modelling software can be used to analyse water flow, heat and solute transport in different saturate mediums using a finite differences approach. HYDRUS uses the McNeal (1968) equation to determine a hydraulic reduction scaling factor, which is also affected by the soil pH. Within HYDRUS, the hydraulic reduction scaling factor is highly sensitive to pH, which does not reflect the actual occurrence in the field (Bennett et al. 2015). Additionally, the McNeal (1968) analytical model was shown to improve where a semi-empirical approach (Ezlit et al. 2013) was used on the basis of C_{TH} being soil specific and not readily predicted. For these reasons, the HYDRUS model does not account for soil-specificity with enough accuracy to allow management recommendations around C_{TH}.

The change of soil structure on a soil-specific basis was ignored in most of these models. Furthermore, evaluation of these models in either laboratory or in field conditions is limited (Šimunek & Suarez 1997). They are designed to work with a given water quality rather than a given soil, hence, none of these models are truly predictive, and the requirement remains to remedy this.

2.6.2 The semi-empirical disaggregation model

The McNeal (1968) clay swelling model was created to quantify the changes that can occur to hydraulic conductivity under sodic soil conditions. By creating a sigmoidal function, the logarithm of the solute concentration can be related to the relative saturated hydraulic conductivity at a given level of sodicity. McNeal (1968) subsequently used the concept of a swelling factor to determine the rK_{sat} with changes in solution concentration and Na. Through the use of a relationship between the hydraulic conductivity and the swelling factor, the McNeal clay swelling model provides relative hydraulic conductivity at various combinations of solute concentrations and ESP.

Ezlit et al. (2013) reanalysed the McNeal (1968) clay swelling model and found that the model had limitations. The first major limitation was that the McNeal's model assumed that the expanding clay will always be 10% of the soil. Secondly, the parameters stated in McNeal's clay swelling model were not given a specific identity.

The use of generalised parameters for different soils were not going to be able to accurately predict the changes in hydraulic conductivity (Ezlit et al. 2013; Šimunek & Suarez 1997). It was more likely to describe the changes that would occur due to infiltration under specific set of conditions instead. The final major issue with the McNeal model was that the decline in hydraulic conductivity in terms of exchangeable Na was marked as the threshold point.

To overcome these limitations, Ezlit et al. (2013) developed a modified model that clarified the boundary between flocculation and disaggregation conditions by using a soil specific form of ESP and empirically fitting parameters relating to the effect of generic clay swelling. The model was validated with soils from the dataset specified in McNeal (1968), as well as against new data. The model was well validated for both smectitic and non-smectitic soils (Ezlit et al. 2013). Thus, the 'clay swelling model' was considered a 'disaggregation model' for all soils, where disaggregation results from intra- and inter- crystalline swelling. The Disaggregation model (Ezlit et al. 2013) relates steady state hydraulic conductivity occurring for a given SAR and EC to formulate the 3-dimensional hydraulic reduction surface using observed data from laboratory leaching columns to account for soil specificity. The formula (Equation 2.21) representing the flocculation condition and disaggregation condition are stated as:

Flocculation condition:

$$RK_{sat} = 1, at\ x \leq 0 \qquad \text{Equation 2.21}$$

Disaggregation condition:

$$RK_{sat} = 1 - \left[\frac{ge^{m\frac{ESP}{100}(x_0)\left[\left(\frac{ESP}{100}\right)^a + b\right]}}{\left\{1 + ge^{m\frac{ESP}{100}(x_0)\left[\left(\frac{ESP}{100}\right)^a + b\right]}\right\}} \right] \text{ at } x > 0 \qquad \text{Equation 2.22}$$

where, rK_{sat} is saturated hydraulic conductivity; *ESP* is exchangeable sodium percentage; x_o is the adjusted effective swelling factor which takes account of swelling and DDL development that controls rK_{sat} dynamics; and, *a, b, g, m* are all optimisable empirical fitted parameters dependent on soil type. This model is semi-empirical, relying on observed data, meaning it is not capable of predicting the soil-specific

response of C_{TH} directly (Bennett & Raine 2012; Ezlit et al. 2013). Furthermore, the model only considers swelling/dispersive systems as Na and Ca, not incorporating K or Mg. Modification of the approach in this model to account for K and Mg would better describe the soil system. Additionally, there remains requirement to understand the mechanisms controlling mechanisms the soil-specific effect to develop a truly predictive model.

2.6.3 Opportunities

There is a need for a predictive model to be designed that can be used to forecast C_{TH}. This review details changes that have occurred in methodology encompassing analysis of marginal quality water and suggests changes required to the methods. Movement towards prediction, or simplified/automated methodology for C_{TH}, would reduce analysis costs and provide confidence in MQSS water as a strategic resource for partitioners and regulators alike. The Ezlit et al. (2013) method for C_{TH} determination is time-consuming and laborious method but provides the best level of information for management. Alternative methods, such as dispersive potential, should be evaluated against this. There is further requirement to assess laboratory output from C_{TH} recommendations against the long-term result of irrigation with MQSS water.

Soil sodicity work has mostly focused on the presence of Na within soil. However, work undertaken by my different researchers (Bennett et al. 2016a; Rengasamy & Churchman 1999; Rengasamy & Marchuk 2011; Smith et al. 2015) has shown that the presence of K and Mg needs to be accounted for when analysing soil response to a given water quality. Design of methodology needs to be changed to incorporate the effect of K and Mg within C_{TH} assessment.

To be able to create a new method or improve an existing method, it is crucial to understand the mechanisms controlling the soil-specific response of a soil to a given water quality. The C_{TH} is clearly demonstrated as soil-specific and universal equations not appropriate for use in terms of the size of the standard deviation observed. The C_{TH} varies with soil type (Quirk 2001; Rengasamy & Olsson 1991), with the key soil properties known to affect the permeability being clay content (Frenkel et al. 1978; McNeal & Coleman 1966), mineralogy (Churchman et al. 1993) and organic matter type and content (Nelson & Oades 1998). The presence of carbonates and oxides (Deshpande et al. 1964), the clay content (Frenkel et al. 1978; Goldberg et al. 1991;

McNeal & Coleman 1966) and type/amount of organic matter (Nelson & Oades 1998) (Murphy 2015) are all suggested to affect aggregate stability. Of all these elements, only clay content was shown to have any direct effect on the soil-specific occurrence of the C_{TH}. The zeta potential, or net negative charge, associated with clay particles essentially takes into account clay mineralogy and charge density effects and therefore presents as a parameter for investigation.

2.7 Conclusions

Increasing pressure on the agricultural industries to produce at a greater rate with lesser number of available resources has led to an emphasis on the investigation of better or alternative methods to fill the gap between the resource supply and demand. This requires an improved use of existing water resources as there are threats to the viability of current irrigation practices. Use of MQSS water for irrigation has been on the rise, although there is caution associated with its use in terms of soil structural decline. Maintenance of soil structure within reasonable hydraulic conductivity rates is possible where the C_{TH} is determined. However, the C_{TH} is clearly soil-specific and difficult (time and expense) to determine. Opportunities exist to improve the methodology through simplification and evaluation against other metrics.

Development of a predictive method would provide the best outcome, but is required to be sufficiently rigorous to not result in undue environmental degradation. As yet, current models do not allow this. Therefore, there remains a requirement to investigate the controlling mechanisms and to incorporate the full range of dispersive characteristics occurring in soils (e.g. K and Mg effects). This review has identified that ionicity and clay domain concepts have merit in being combined with quantitative measures of clay mineralogy to explain the soil specific effect.

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3 Validating laboratory assessment of threshold electrolyte concentration for fields irrigated with marginal quality saline-sodic water

Dang, A[1], Bennett, J. McL[1], Marchuk, A[1], Marchuk, S[1], Biggs, A.J.W[2], and Raine, S.R[1]*

[1] *University of Southern Queensland, West St, Toowoomba, QLD 4350, Australia*

[2] *Department of Natural Resources and Mines, Tor St, Toowoomba, QLD 4350, Australia*

[*] *Corresponding author: John.Bennett@USQ.edu.au*

3.1 Abstract

The use of marginal quality saline-sodic (MQSS) water for agricultural production is important in water limited environments and with growing demand for food and fibre. Soil structural response to irrigation water quality is known to be a function of sodium contained in the irrigation water and the electrolyte concentration of that water. The threshold electrolyte concentration (C_{TH}) is classically used to determine the suitability of water to be applied to a soil, and is usually conducted as a laboratory analysis utilising saturated hydraulic conductivity. This work aimed to validate the laboratory based semi-empirical disaggregation model approach to C_{TH} against field soils where MQSS water had been applied for an extended period of time. Unirrigated locations proximal to long-term irrigation sites were paired to provide control conditions and the C_{TH} was determined. Reduction in hydraulic conductivity from the control was determined as both observed and predicted data. Results supported validation of the approach, indicating the disaggregation model as useful for proactive planning of irrigation systems with regard to water quality and a good measure for identification of MQSS water as a strategic resource. Applicability of the results to irrigation guidelines was discussed with particular focus on removal of generalised guidelines and identification of what constitutes tolerable hydraulic conductivity reduction.

Keywords: dispersion, swelling, aggregate stability, threshold turbidity concentration

3.2 Introduction

Marginal quality saline-sodic (MQSS) water is an important resource for agricultural irrigation, be it groundwater, or industry by-product water (Qadir & Oster 2004). Such waters are generally high in Na, which may cause irreparable soil structural issues via

the exchange and equilibrium processes that occurs between the soil soluble and solid phases (Ezlit et al. 2010; Raine et al. 2007; Rengasamy & Olsson 1993). The ensuing instability of soil aggregates leads to clogging of pores, a reduction in soil hydraulic conductivity, reduced nutrient movement and eventual productivity decline (So & Aylmore 1993). Where the electrolyte concentration (directly proportional to electrical conductivity; EC) is high enough to maintain the clay domain via osmotic compression of the diffuse double layer, the hydraulic conductivity and infiltration rate can be maintained to a reasonable extent, albeit still reduced compared to a Ca saturated system (McNeal 1968; Quirk & Schofield 1955; Shainberg & Letey 1984). Therefore, the ability of soil to receive MQSS water is a function of both the Na concentration and the EC.

Quirk and Schofield (1955) demonstrated that permeability of a soil irrigated with high sodium adsorption ratio (SAR) solution could be maintained provided that the EC was sufficiently high. Notably, where Ca saturated clays were investigated, reduction in EC did not cause hydraulic decline, but maintained a relatively consistent clay platelet spacing, which they termed as a potential minima (absolute stability). On the other hand, the introduction of Na into the system resulted in a gradual decline of hydraulic conductivity and was highly sensitive to reduction in EC. They subsequently defined the threshold electrolyte concentration (C_{TH}) as a 10% reduction in saturated hydraulic conductivity (rK_{sat}) from the absolute stability condition. Importantly, from the condition of absolute stability the clay domain gradually expands due to disaggregation processes (intracyrstalline swelling and diffuse double layer development) approaching the threshold turbidity concentration (C_{TU}), which is beyond the C_{TH} and represents the aggregation–dispersion boundary. This insinuates that the rK_{sat} occurring up to the C_{TU} is due to somewhat reversible processes, as dispersion has not yet occurred, which was the premise of the disaggregation model of Ezlit et al. (2013) based on the work of McNeal and Coleman (1966). Ezlit et al. (2013) define the C_{TH} as rK_{sat}=20% on the basis that departure from absolute stability occurs gradually with Na addition and that the reduction needs to be beyond the measurement error. This concept is applied for beneficial use of industry by-product water (Bennett et al. 2016b; Bennett & Warren 2015; Smith et al. 2015) and is applicable to agricultural water management (Agassi et al. 1981; de Menezes et al. 2014; Frenkel et al. 1978; Marchuk & Rengasamy 2012).

Of great importance is the fact that the C_{TH} is soil-specific (Bennett & Raine 2012; Marchuk & Rengasamy 2012; McNeal & Coleman 1966). This implies that soil characteristics must be understood in order to properly predict the response of a particular soil to MQSS water, meaning that modelling approaches based on water quality parameters alone, such as Mallants et al. (2017a) and Mallants et al. (2017b) have considerable potential to result in environmental harm for some soils. The ability to predict the soil-specific response to MQSS application does not yet exist, despite mathematical investigations (Mau & Porporato 2015) and semi-quantitative clay mineralogical suite investigations. The semi-empirical disaggregation model (Bennett et al. Submitted) compromises between direct measurement of the C_{TH} and complete prediction, relying on rK_{sat} from small core experiments within the laboratory.

While there is some short-term evidence for laboratory C_{TH} assessment reliability in the field (Bennett et al. 2016b), it would be desirable to produce a greater body of evidence for longer-term irrigated sites. Given that the C_{TH} varies with soil type, and that clay content (Frenkel *et al.* 1977; Goldberg *et al.* 1991; McNeal *et al.* 1966), clay mineralogy (Churchman *et al.* 1995), carbonates (Chorom & Rengasamy 1997), iron oxides (Deshpande et al. 1964; Goldberg 1989), as well as organic matter type and content (Nelson and Oades 1998) are suggested to affect C_{TH}, irrigation with MQSS water under field conditions may have unexpected results. Field conditions are very rarely saturated, except in subsoils, poor irrigation management and within the very near surface during furrow irrigation (Raine et al. 2007), existing as unsaturated environments, which presumably would affect equilibrium conditions. Furthermore, the timescale of the semi-empirical assessment of C_{TH} occurs over a much shorter timescale than the evolution of field soil structure under irrigation with MQSS water and regional rainfall (Minhas 1996). On this basis, the aim of this study was to validate C_{TH} laboratory assessment against soils that had been irrigated with MQSS water for multiple years.

3.3 Methodology

3.3.1 Experimental design

This work uses uncultivated and unirrigated soil proximal to long-term cultivated and irrigation sites as the basis of comparison. The principal issue in validating the Ezlit et al. (2013) approach is that direct measurement under field conditions would require the saturated hydraulic conductivity to be assessed initially as a benchmark condition

prior to an irrigation regime commencing and these points within a field tracked over multiple seasons. Field variability, compaction due to traffic and shrink-swell structural conditions would all introduce error. However, the direct in-field comparison of uncultivated land to cultivated and irrigated land presents confounded conditions in terms of soil hydraulic network continuity and bulk density. For this reason, soils were sampled from either irrigated or unirrigated regions, homogenised (within region, not between region), and then brought back to the laboratory for comparison as reconstituted cores.

The unirrigated soil samples were used for C_{TH} assessment consistent with the method of Ezlit et al. (2013). All soil samples were taken uniformly from 0–0.2 m to ensure the highly dynamic surface conditions (influenced greatly by small rain events) did not override the long-term unsaturated conditions Replicated subsamples (5) of each irrigated soil were wet to a nominal field capacity of -10 kPa using a hanging column and then subject to centrifuge drainage to obtain the soil solution at this suction, consistent with the method described in Bennett et al. (2016b). These data were used to prepare field condition equilibrium treatment irrigation solutions. Additionally, irrigation water records over the lifetime of irrigation application were used to produce a weighted mean water quality treatment; weighted in terms of poorest quality as a function of magnitude of application. The true equilibrium condition would lie between the field condition equilibrium solutions and the weighted mean irrigation water qualities. Hence, these treatments were used to generate a steady state saturated hydraulic conductivity and subsequently compared to the C_{TH} assessment of unirrigated soils to test the hypothesis and seek to validate the Ezlit et al. (2013) approach.

3.3.2 Soil selection and characteristic analysis

Eight cotton farms in Queensland (Table 3.1) that had undertaken irrigation with marginal quality water were selected. From each farm, a sample was collected from the irrigated site, and a sample was also collected from a nearby plot that had never been irrigated. Bulk sample to fill a 44 gallon drum was taken from throughout the field using a uniform sampling method of collecting the topsoil with a shovel to provide a representative sample. A total of 16 soil samples (two from each farm) were collected from 0–0.2 m depth, air-dried (40° C) and gently ground to pass a 2 mm sieve.

Table 3.1. GPS locations of the eight soils used in this experiment given in southing and easting

Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7	Soil 8
-27.022, 151.126	-27.23, 151.32	-27.077, 151.134	-27.037, 151.125	-27.020, 151.167	-27.969, 148.381	-28.945, 150.606	-28.956, 150.619

Soil pH and electrical conductivity (EC) were determined in 1:5 soil: deionised (DI) water using a Radiometer analytical ION 450 Meter. Total organic carbon was measured on LECO (Rayment & Lyons 2011). Exchangeable cations were determined using a Perkin Elmer NexIon-ICP MS (Inductively Coupled Plasma – Mass Spectrometer). For exchangeable cations, the soluble salts were washed out with deionised water and then the samples were extracted with 0.5 M NH_4Cl pH adjusted to 7.2 or 8.2 to match the pH of the soil analysed (Marchuk & Rengasamy 2012). The extractant was centrifuged for 30 mins and analysed on the ICP-MS to calculate SAR (Rayment & Lyons 2011).

The tendency of clay colloids to disperse was assessed as electrophoretic mobility by use of zeta potential (ζ) measured using a Malvern Zetasizer (Marchuk & Rengasamy 2012). For spontaneous dispersion in water, 1:5 soil: DI water suspensions were prepared and upended carefully three times. These were left to sit for 4 hours before extraction of the suspended clay in solution and measurement of this via a Malvern Zetasizer. Turbidity (NTU) was also measured on this clay suspension using a HACH 2100N turbiditimeter. The clay mineral suite was semi-quantitatively determined consistent with the methods presented in Marchuk et al. (2016) using the sedimentation method of Jackson (2005) for clay separation without addition of dispersing agents or chemical treatments (such as for organic matter or oxide removal). Interpretation of data was also consistent with Marchuk et al. (2016) using CSIRO software XPLOT for Windows (Raven 1990) comparing the XRD patterns with the International Centre for Diffraction Data (ICDD) database of standard diffraction patterns using computer aided search/match algorithms.

Table 3.2. Selected physicochemical properties of the 8 soils; U – unirrigated soil initial field conditions; I- irrigated soil initial field conditions; EC- electrical conductivity; TCC – total cation concentration; SAR – sodium absorption ratio; ESP – exchangeable sodium percentage; CEC – cation exchange capacity; ASC – Australian Soil Classification (Isbell 2002)

Soil	*Units*	*Soil 1*		*Soil 2*		*Soil 3*		*Soil 4*		*Soil 5*		*Soil 6*		*Soil 7*		*Soil 8*	
Field state		U	I	U	I	U	I	U	I	U	I	U	I	U	I	U	I
pH		8.57	8.83	7.24	8.74	7.95	8.87	7.98	8.47	7.27	8.92	7.49	7.99	8.44	8.55	8.26	8.60
EC	dS/m	0.10	0.45	0.21	0.13	0.13	0.19	0.36	0.43	0.19	0.30	0.04	0.04	0.96	1.17	0.14	0.17
Organic carbon	%	1.06	0.8	1.01	1.09	1.02	0.95	0.98	1.11	1.31	1.54	0.69	0.92	1.56	1.86	1.02	1.23
Soluble Cations ($mmol_c/L$)	Na	0.86	4.43	0.77	1.05	1.73	1.05	3.66	1.36	1.87	0.57	0.08	0.05	4.66	4.96	1.33	1.01
	Mg	0.63	0.40	0.52	0.31	0.26	0.30	0.38	0.58	0.27	0.70	0.07	0.06	0.71	0.47	0.36	0.34
	K	0.09	0.09	0.10	0.09	0.08	0.10	0.10	0.32	0.10	0.22	0.21	0.23	0.45	0.49	0.09	0.10
	Ca	1.03	0.10	0.76	0.62	0.26	0.45	0.84	0.73	0.45	1.99	0.16	0.24	3.74	2.05	0.49	0.65
TCC	$mmol_c/L$	2.61	5.02	2.16	2.07	2.33	1.91	4.98	3.00	2.69	3.48	0.52	0.59	9.57	7.97	2.27	2.10
Exchangeable Cations ($cmol_c/100g$)	Na	0.40	2.53	0.39	0.14	0.94	2.88	1.03	3.25	3.73	0.93	0.01	0.00	0.14	0.20	0.69	1.00
	Mg	8.67	9.01	2.87	3.53	13.70	11.30	14.81	13.18	14.52	15.47	0.76	0.67	1.72	1.99	11.33	13.58
	K	2.95	1.50	0.66	0.48	1.00	1.32	0.96	0.99	1.12	1.56	0.61	0.91	0.82	0.95	0.81	0.83
	Ca	25.52	25.12	11.66	9.52	20.87	20.31	24.30	24.93	19.87	17.32	2.04	3.61	10.67	9.64	18.35	22.10
CEC		37.54	38.16	15.58	13.67	36.51	35.81	41.10	42.35	39.24	35.28	3.41	5.20	13.35	12.77	31.19	37.51
SAR		0.98	5.84	0.96	1.54	3.36	1.71	4.69	1.68	3.09	0.49	0.23	0.13	3.13	4.42	2.04	1.43
ESP	%	1.07	6.62	2.50	1.06	2.57	8.04	2.51	7.67	9.51	2.64	0.16	0.10	1.03	1.56	2.22	2.66
Texture		Clay		Clay		Clay		Clay		Clay		Sandy loam		Silty clay loam		Silty clay	
ASC		Black Vertosol		Black Vertosol		Black Vertosol		Black Vertosol		Black Vertosol		Red Kandosol		Brown Dermosol		Brown Vertosol	
Clay content	%	75	76	52	58	60	62	61	62	62	63	12	11	23	24	53	52
Zeta Potential	mV	-23	-25	-23	-24	-29	-29	-27	-25	-16	-28	-33	-32	-19	-22	-29	-31

All 5 soils had a two-component clay mineral suite of montmorillonite (d≈15.8 Å) and kaolinite (d≈7.15 Å) dioctahedral types (060 patterns not shown) in addition to accessory minerals anatase (d≈3.52 Å), hematite (d≈2.70 Å) and the primary mineral quartz (d≈3.34 Å). The quantitative estimation of clay phases for all 5 soils are presented in Table 3.3. Mineralogical composition of clays (%) from XRD analysis. No difference between irrigated and unirrigated soils were evident in terms of mineralogy so a single suite is provided below per soil. Soils were generally Montmorillonite dominant, with exception of Soil 2, Soil 6 and Soil 7, which were Quartz dominant.

Table 3.3. Mineralogical composition of clays (%) from XRD analysis. No difference between irrigated and unirrigated soils were evident in terms of mineralogy so a single suite is provided below per soil

Soil	Montmorillonite	Kaolinite	Anatase	Hematite	Quartz
Soil 1	76	10	4	1	9
Soil 2	23	21	4	0	52
Soil 3	72	7	3	1	17
Soil 4	62	6	3	0	29
Soil 5	60	7	4	1	28
Soil 6	1	29	0	0	63
Soil 7	13	34	0	0	53
Soil 8	79	6	0	0	15

Soils 1–5 were all black Vertosols, Soil 6 was a red Kandosol, Soil 7 was a brown Dermosol, and Soil 8 was a brown Vertosol. The soils had varying amounts of organic carbon, soluble cations and exchangeable cations (Table 3.2) thus providing a range of physico-chemical properties to evaluate soil-specific response.

3.3.3 Saturated hydraulic conductivity measurement and solutions

The C_{TH} analysis was conducted as per Ezlit et al. (2013) for the unirrigated soils using two soil core replicates per soil, and assessed via saturated hydraulic conductivity. The benchmark conditions (absolute stability) was determined using a $CaCl_2$ solution prepared at EC 2. The soil cores were then designed to be fixed at (EC: 0.5, 1.0, 2.0, 4.0, or 8.0 dS/m) each and progressive treatment solutions were applied with increasing SAR (Table 3.4). Steady state conditions were obtained for each treatment solution applied during C_{TH} assessment, defined as less than 3% variation in the volume between consecutive measurements after a 10 min interval for at least 1h (Reading et al. 2012). During the entire experimental process soil cores were kept

saturated. The rK_{sat} was calculated for each soil core used to create a three dimensional response surface using TableCurve 3D (SYSTAT Software Inc. 2002) for rK_{sat} as a function of solution SAR and EC.

Absolute stability condition:

$$rK_{sat} = 1, at\ x \leq 0 \qquad \text{Equation 3.1}$$

Disaggregation condition:

$$rK_{sat} = 1 - \left[\frac{ge^{m\frac{ESP}{100}(x_0)\left[\left(\frac{ESP}{100}\right)^a + b\right]}}{\left\{1 + ge^{m\frac{ESP}{100}(x_0)\left[\left(\frac{ESP}{100}\right)^a + b\right]}\right\}}\right] \text{ at } x > 0 \qquad \text{Equation 3.2}$$

where rK_{sat} is the reduction in saturated hydraulic conductivity; *ESP* is exchangeable sodium percentage; x_o is the adjusted effective swelling factor which takes account of the swelling and dispersion that controls rK_{sat} dynamics; and, *a, b, g, m* are all optimisable empirical fitted parameters dependent on soil type.

Table 3.4. Required amounts of NaCl and $CaCl_2$ for solution preparation for EC sequence 0.5, 1, 2, 4 and 8 dS/m; SAR, sodium adsorption ration; Treat, treatment; TCC, total cation concentration

SAR curve.	*Na* ($mmol_c/L$)	*Ca* ($mmol_c/L$)	SAR ($mmol_c/L$)	*Final TCC* ($mmol_c/L$)	*SAR Curve*	*Na* ($mmol_c/L$)	*Ca* ($mmol_c/L$)	SAR ($mmol_c/L$)	*Final TCC* ($mmol_c/L$)
	0	80.00	0	80		75.00	5.00	47.43	80
	0	40.00	0	40		37.50	2.50	33.54	40
0	0	20.00	0	20	**5**	18.75	1.25	23.72	20
	0	10.00	0	10		9.37	0.63	16.77	10
	0	5.00	0	5		4.69	0.31	11.86	5
	30.00	50.00	6.00	80		77.00	3.00	62.87	80
	15.00	25.00	4.24	40		38.50	1.50	44.45	40
1	7.50	12.50	3.00	20	**6**	19.25	0.75	31.43	20
	3.75	6.25	2.12	10		9.62	0.38	22.23	10
	1.87	3.13	1.50	5		4.81	0.19	15.72	5
	50.00	30.00	12.91	80		78.10	1.90	80.12	80
	25.00	15.00	9.13	40		39.05	0.95	56.66	40
2	12.50	7.50	6.45	20	**7**	19.52	0.48	40.06	20
	6.25	3.75	4.56	10		9.76	0.24	28.33	10
	3.12	1.88	3.23	5		4.88	0.12	20.03	5
	63.00	17.00	21.61	80		78.80	1.20	101.72	80
	31.50	8.50	15.28	40		39.40	0.60	71.93	40
3	15.75	4.25	10.80	20	**8**	19.70	0.30	50.86	20
	7.87	2.13	7.64	10		9.85	0.15	35.97	10
	3.94	1.06	5.40	5		4.92	0.08	25.43	5
	71.00	9.00	33.47	80		80.00	0	∞	80
	35.50	4.50	23.67	40		40.00	0	∞	40
4	17.75	2.25	16.73	20	**Infinity**	20.00	0	∞	20
	8.87	1.13	11.83	10		10.00	0	∞	10
	4.44	0.56	8.37	5		5.00	0	∞	5

For the irrigated soils, both the field capacity and groundwater irrigation solutions were prepared on a soil-specific basis, as outlined in the experimental design. Soil cores were prepared as for C_{TH} analysis, with five replicates per treatment, per soil (ten cores per soil). Solutions were prepared to reflect the SAR and EC of the water available to each of the farmers from their bores. Soil cores were saturated slowly from the bottom over a period of one hour, after which they were removed and placed into leaching racks where a constant hydraulic head was applied using the respective treatment solution. These soils were run with this solution until steady state was achieved using the same definition as per C_{TH}.

Table 3.5. EC and SAR of solutions used to calculate the reduction in hydraulic conductivity after irrigating with marginal quality water

Soil	Soil-water solution		Irrigation solution	
	EC (dS/m)	SAR	EC (dS/m)	SAR
1	3.64	10.98	2.28	8.35
2	0.87	3.41	2.57	14.39
3	0.89	3.38	3.61	12.46
4	0.71	4.71	3.94	12.20
5	1.96	8.25	2.67	14.33
6	0.61	1.04	2.25	14.32
7	0.83	7.40	0.72	15.15
8	0.85	2.66	0.60	2.92

The $CaCl_2$ benchmark conditions of the unirrigated soil were used to determine the expected benchmark conditions for the irrigated soils fixed at the respective treatment EC using the following equation (Table 3.6)

$$K_{sat} = a \ln EC + b \qquad \text{Equation 3.3}$$

Where K_{sat} is the saturated hydraulic conductivity at the benchmark condition respective to the solution electrical conductivity (EC), which was determined as either the soil solution or irrigation solution EC depending on the treatment. Parameters 'a' and 'b' are optimisable parameters determined by the soil specific response to $CaCl_2$ (over EC=0.5–8.0 dS/m) for the unirrigated soils. The observed steady state saturated hydraulic conductivity was subsequently used with the expected benchmark condition and reduction in hydraulic conductivity calculated.

Table 3.6. Benchmark condition equations for the eight soils obtained from the $CaCl_2$ solutions of the soils with unirrigated initial field condition where variables '*a*' and '*b*' from Equation 3 have been parameterised on a soil-specific basis

Soil	Equation
Soil 1	K_{sat}=8.5883ln(EC)+57.466
Soil 2	K_{sat}=40.823ln(EC)+119.13
Soil 3	K_{sat}=19.556ln(EC)+47.018
Soil 4	K_{sat}=32.570ln(EC)+47.719
Soil 5	K_{sat}=8.8717ln(EC)+31.844
Soil 6	K_{sat}=6.9844ln(EC)+56.134
Soil 7	K_{sat}=1.7576ln(EC)+22.414
Soil 8	K_{sat}=0.7088ln(EC)+15.365

3.4 Modelling

TableCurve 3D software facilitated the modelling of data into a three dimensional surface using the Equation 3.1 and Equation 3.2 for hydraulic reduction (Ezlit et al. 2013). For all eight soils, data from the C_{TH} analysis was modelled using TableCurve 3D. The 20%, 40%, 60% and 80% rK_{sat} contour were extracted and plotted for each soil. TableCurve input parameters for the Ezlit et al. (2013) equation and the associated model statistics are provided in Table 3.7.

3.5 Results

3.5.1 Threshold electrolyte concentration analysis of the unirrigated soils

For the eight soils, at least 80% of the variation in rK_{sat} was explained by the fitted surface as a function of ESP and EC, with the majority of the soils having >90% of the variation explained (Table 3.7). Deviation of the surface from the data points is depicted in Figure 3.1. The predicted R^2 for the eight soils provides a very good indication of predictive capability of the surface for non-data point regions within the bounds. Additionally, the fitted standard errors for the eight surfaces are small. These statistics indicate that the surfaces explain the data well and are useful for prediction of rK_{sat} for changes in irrigation water quality.

Soil 6, a red Kandosol, and Soil 7, a brown Dermosol, had rK_{sat} at SAR=infinity of 80% and 60% respectively at high EC solutions, indicating a greater resilience to dispersion; the remaining soil's rK_{sat} decreased by >95% at the same solution. Such results may be consistent with the high sand content of the Kandosol, whereby clay dispersion even at extreme SAR is insufficient to completely block conducting pores.

At the brown Dermosol site there was an abundance of ironstone, which may support resistance of aggregates to dispersion due to iron oxides. This reasoning was unable to be tested, but is presented here as a matter of consideration; as discussed above, the disaggregation model fitted surface and predictive capability for both soils was very good.

The C_{TH} of the soils varied between soil classification and within the Vertosol classification (Figure 3.1 and Figure 3.2). Soil 4, a black Vertosol, had very rapid reduction to rK_{sat}=20%, with the C_{TH} curve (Figure 3.2) substantially different to the other 5 Vertosols which could be due to its high initial SAR and CEC.

Table 3.7. Model parameters for the fitted surface predicted through TableCurve

Model parameters	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7	Soil 8
a	0.514	1.723×10^{-4}	0.459	0.512	0.96	0.379	0.068	2.278×10^{-6}
b	2	1.919	1.319	0.466	1.999	1.692×10^{-6}	0.391	0.423
g	38	0.426	13.96	11.676	14.579	0.556	2.626	3.821
m	7.117	13.769	5.594	4.415	9.932	5.034	0.756	8.605
s	1.154	4.032	0.077	5.106×10^{-5}	1.887	2.347	7.001	7.733
l	-4.708	-28.604	-0.681	1.592×10^{-5}	-11.31	0.387	-11.27	-20.23
F value	0.363	0.783	0.515	0.143	0.276	0.079	0.086	0.054
R^2	0.962	0.967	0.928	0.854	0.969	0.843	0.80	0.89
Predicted R^2	0.956	0.961	0.915	0.827	0.964	0.813	0.752	0.871
Fitted standard error	0.014	0.011	0.006	0.036	0.070	0.056	0.012	0.013

3.5.1 Reduction in soil hydraulic conductivity of the irrigated soils

Figure 3.2 depicts the soil-water and irrigation solutions used to assess the rK_{sat} due to the use of MQSS water, with the true reduction existing on the line bounded by these points. For Soils 2–6 the soil-water solution had both a lower SAR and EC than the irrigation solution, indicating that the soil water system was diluted within the top 0.1 m of the soil. Soil 1 and 8 had the reverse, with the soil-water solution having both SAR and EC greater than for the irrigation solution, consistent with solute concentration within the top 0.1 m of soil. Soil 7 soil-water solution had a lower SAR and higher EC than for the irrigation solution; this may suggest initial dilution followed by concentration due to rainfall and evaporation sequences. The true rK_{sat} was therefore, predicted with variation between soil-water and irrigation solutions of 3–17%, which corresponded to variation for observed soil-water and irrigation solution variation of 1–19%.

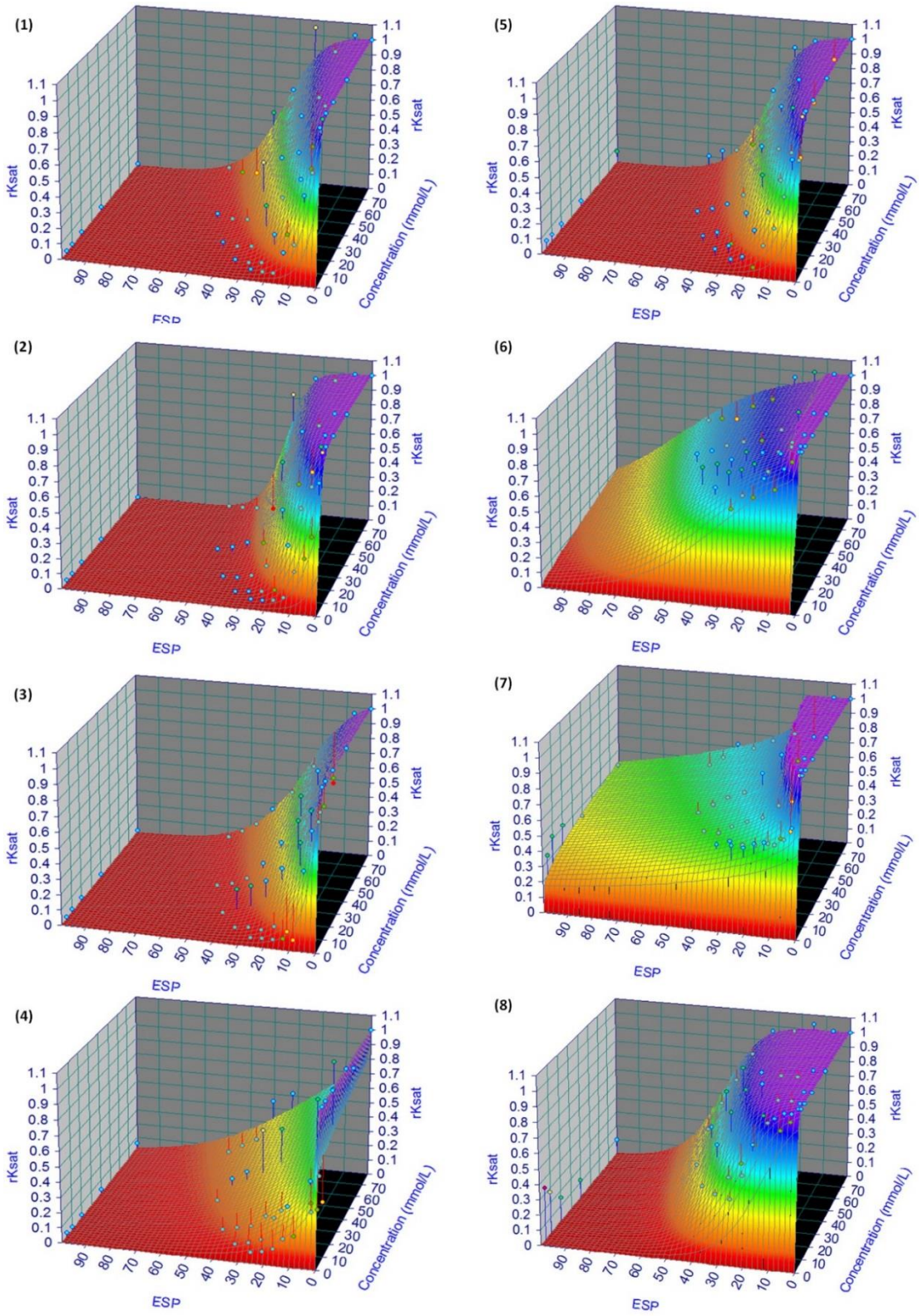

Figure 3.1. Reduction in saturated hydraulic conductivity (rKsat) for eight southeast Queensland soils (1–8). The 3-Dimensional surfaces are function of the exchangeable sodium percentage (ESP) and solution concentration (mmolc/L) as calculated using the approach of Ezlit et al. (2013). Model parameters and associated statistics are presented in

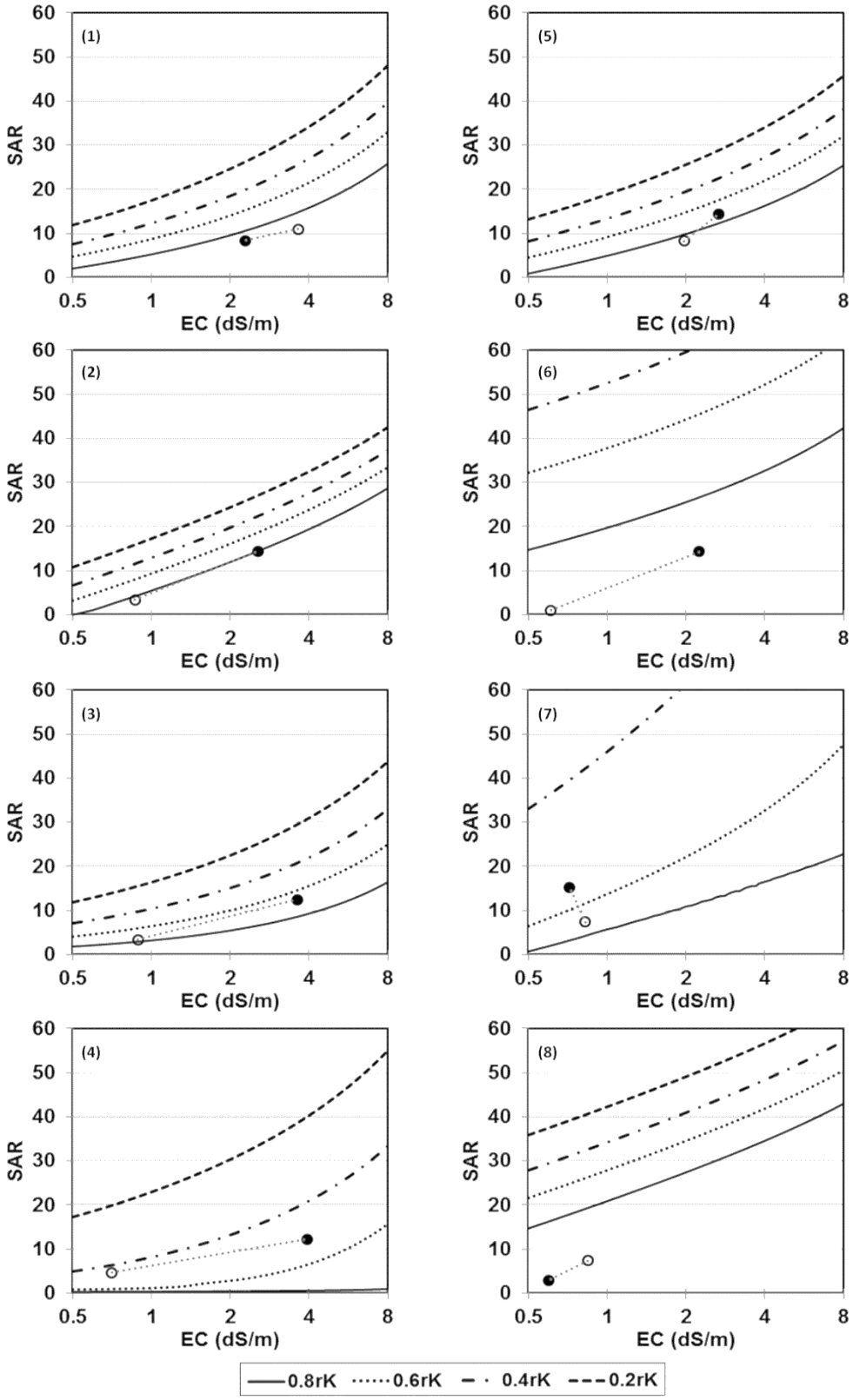

Figure 3.2. Reduction in saturated hydraulic conductivity (rK_{sat}) as a function of solution sodium adsorption ratio (SAR) and electrolyte concentration (EC). Threshold electrolyte concentration is defined as a 20% reduction in hydraulic conductivity (0.8rK). The hollow circle represents the soil solution and the solid circle represents the irrigation solution, with the true field condition existing on the hashed line between these points; 0.2rK curves for Soil 4, 6 and 7 occur at SAR greater than the graphical domain presented.

The observed rK_{sat} for the eight soils ranged from 1–87%, while the predicted rK_{sat} ranged from 2–66%. This discrepancy was due to Soil 3 where the observed rK_{sat}=87 and 83% as compared to the predicted rK_{sat}=21 and 34% for the soil-water and irrigation solution treatments, respectively. This resulted in an observed to predicted rK_{sat} difference of 66% and 48% for the soil water and irrigation solution treatments, respectively. For all other soils, the difference between the observed and predicted results for soil-water and irrigation solution treatments was <9%. For this reason, Soil 3 was considered an outlier and was removed from the direct comparison of observed and predicted data used for model validation (Figure 3.3). While Soil 3 was removed from the validation data set these points are still depicted in Figure 3.3 in order to demonstrate how different they were from the remaining 7 independent soil samples. The regression line for the 7 soils was very close to the 1:1 observed versus predicted data line (gradient of 0.97) and explained 96% of the data variation indicating a very good fit. Therefore, these data support validation of the model results.

Table 3.8. Reduction in hydraulic conductivity from benchmark conditions after irrigation with two different treatments; Benchmark – benchmark condition saturated hydraulic conductivity determine using $CaCl_2$ to represent the most stable condition of the soil at a given electrical conductivity K_{sat} – saturated hydraulic conductivity; rK_{sat} – reduction in saturated hydraulic conductivity; Pred – predicted; Obs Treat Range, Pred Treat Range – rK_{sat} variation between soil-water and irrigation solutions (Treat) as observed (Obs) and predicted (Pred); Difference – difference between the observed and predicted rK_{sat}

Soil	Treatment	Benchmark (mm/h)	K_{sat} (mm/h)	rK_{sat} (%)	Pred rK_{sat} (%)	Obs Treat Range (%)	Pred Treat Range (%)	Difference (%)
1	1	69	55	20	18	8	3	1.8
	2	65	57	12	15			3.3
2	1	113	89	21	19	2	3	2.4
	2	158	121	23	22			1.2
3	1	13	2	87	21	4	13	66.1
	2	21	4	83	34			48.7
4	1	36	13	64	66	8	16	1.7
	2	92	40	57	50			6.7
5	1	38	28	27	19	1	10	8.3
	2	41	29	28	29			0.9
6	1	53	52	1	3	19	13	1.7
	2	62	49	21	16			4.7
7	1	37	25	32	28	17	17	3.9
	2	24	12	49	45			4.3
8	1	16	14	10	2	7	14	8.2
	2	16	13	17	16			1.4

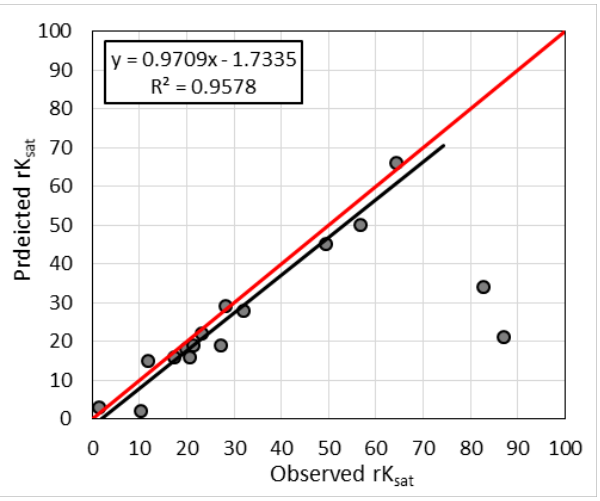

Figure 3.3. The reduction in hydraulic conductivity as predicted using threshold electrolyte concentration analysis semi-empirical modelling for previously unirrigated soils versus the observed reduction in saturated hydraulic conductivity for soil previously irrigated with marginal quality saline sodic water. The diagonal red line represents the 1:1 line, while the black line is the regression fit for the observed data ignoring the two outliers.

3.6 Discussion

3.6.1 Model validation

With the exception of the observed results for Soil 3, the results support validation for the use of the Ezlit et al. (2013) disaggregation model in determining the C_{TH} with relevance to field application of MQSS water. It is likely that Soil 3 was subject to irrigation with MQSS groundwater followed by irrigation with good quality, low EC, captured rainfall. Thus, removal of the data as an outlier was warranted, especially given the obvious trend of the remaining 7 soils. From Table 3.1 and Table 3.2 the key parameters of CEC, clay content, mineralogy and Australian Soil Classification were used to determine the similarity of the proximally located irrigated and unirrigated soil samples. In all cases, no significant differences were found between irrigated and unirrigated soils for these parameters, confirming that the soils were fair in comparison. Therefore, given the relationship between observed and predicted rK_{sat} (R^2=0.96) in Figure 3.3, it is deduced that laboratory assessment of C_{TH} is relevant in informing changes in field conditions. Similar results were obtained by Bennett et al. (2016b) for reuse of coal seam gas water on a red Vertosol where no significant change in K_{sat} was observed for soil irrigated with SAR=24 and EC=3.2 dS/m, as predicted by C_{TH} analyses carried out for that site.

In the current work, it was not feasible to identify new areas for irrigation and then subject these to irrigation with MQSS water. For this reason the experimental design

focused on proximally paired sites that were subsequently relocated and reconstituted as short leaching columns. We acknowledge that the soils *in situ* would not be subject to saturated conditions under the majority of rainfall and irrigation events, but contend that the true soil-water concentration and cation suite is reflected by the experimental approach in this work. In the case of Bennett et al. (2016b), the C_{TH} was conducted to inform water treatment targets for application to land, prior to irrigation system installation and operation. Their results therefore, directly tracked *in situ* changes throughout time. Shainberg and Letey (1984) suggest that the soils irrigated with MQSS water in a laboratory are usually more sensitive than those within a field, which may have occurred in the Red Vertosol of Bennett et al. (2016b). The current work might be furthered by use of intact large columns (large to account for macroposrosity variation spatially). However, we suggest that the validation of the disaggregation model still holds as the use of laboratory soil cores, while potentially more sensitive than *in situ* field soils, at an rK_{sat}=20% as the reduction threshold provides a safety factor protecting soils from undue degradation (Quirk 2001).

3.6.2 Soil-specific threshold electrolyte concentration

The results for the eight soils provide further evidence for the C_{TH} being soil-specific, even within the same soil classification and where soil characteristics such as pH, organic matter, clay content, CEC and mineralogical suite were highly similar for the Vertosol soils. Quirk and Schofield (1955) and Quirk (1971) initially suggested that the C_{TH} relationship was universal and able to be described by a generalised equation. Various authors (Bennett & Raine 2012; Marchuk & Rengasamy 2012; McNeal 1968; McNeal & Coleman 1966; Shainberg & Letey 1984) have demonstrated that a universal approach to describing C_{TH} is not appropriate. Quirk (2001) later concedes that variation in C_{TH} should be expected, but that the equations presented by Quirk and Schofield (1955) describe the general relationship. For the Vertosol soils in this work, Soils 1, 2, 3, 5 and 8 generally have similar C_{TH}, although the standard error for the relationships was by and large SAR>± 6.8. Such variation from a general relationship may have significant practical implications. Importantly, Soil 4, was distinctly different from the remaining Vertosols in its C_{TH}, but highly similar in terms of its physical, chemical and mineralogical characteristics. We contend that intricacies within the mineralogy likely explain this result, demonstrating that future work should seek to quantifiably determine clay mineralogy, its size range, and differences in

charge interactions. Use of a general relationship for such a soil would likely result in 50–60% rK_{sat}. Hence, use of the disaggregation model with soil-specific observed data to inform irrigation of MQSS water is advised.

3.6.3 Irrigation and soil management implications

Validation of the Ezlit et al. (2013) semi-empirical disaggregation model for the field soils suggests that irrigation systems can be adequately planned for in terms of water quality and soil structural degradation. Current guidelines for Australian irrigation (ANZECC 2000) utilised generalised equations for the use of MQSS water, which is advised against by both literature and the results of this work. Similar to general use guidelines for wastewater and groundwater associated with the coal seam gas industry, it would be advisable to set a lower limit for SAR at a specified EC where the 80–90% have rK_{sat}<20% with the majority of the remaining soils (e.g. Soil 4) not decreasing by >40%.

Shainberg and Letey (1984) proposed the use of an rK_{sat}=50% as the C_{TH} on the basis that laboratory testing of soils is generally more sensitive than for the same soils under field condition. However, this assertion is made on a limited data set and with the assumption that the selection of the rK_{sat} is arbitrary. While the rK_{sat} is somewhat arbitrary, it is linked to physicochemical phenomena, whereby K_{sat} reduction is gradual as sodium concentration increases and/or electrolyte concentration decreases, and the stability condition departs occurs from is a potential minima (Quirk 2001). The initial selection of rK_{sat}=10% (Quirk & Schofield 1955), and the current use of rK_{sat}=20% (Ezlit et al. 2013), are based on measureable departure from this potential minima taking into account the extent of error associated with the measurement method, while seeking to limit undue soil structural deterioration. Increasing the rK_{sat} that defines the C_{TH} is a worthy discussion in terms of ability to use MQSS water as a strategic irrigation resource, particularly in water limited environments. Shainberg and Letey (1984) and de Menezes et al. (2014) both pointed out that if initial K_{sat} is substantial, then rK_{sat}>>20% may well be tolerable. However, the definition of tolerable requires further consideration. Quirk (2001) wrote his review with a particular focus on misunderstanding of the C_{TU}, which occurs at the aggregate-dispersion boundary and is considered to be where hydraulic reduction is no longer reversible to any extent. This definition acknowledges that intercyrstalline swelling is a reversible process, as is the development of a diffuse double layer (intracyrstalline swelling), provided the

diffuse double layer does not overcome the attractive forces within the clay domain. On this basis, we emphasize that '*tolerable*' reduction in K_{sat} could be defined as the rK_{sat} occurring at the C_{TU}. However, caution is needed in this approach as there is no safety buffer, which the C_{TH} effectively provides (Quirk 2001). Rapid dilution during rainfall could completely negate the aggregated condition, under such definition of '*tolerable*', and result in irreparable damage even where systems are buffered with an electrolyte source, such as gypsum (Ali & Watson 2018). It is worth noting that the C_{TU} occurs at approximately rK_{sat}=56% at SAR=21 in the pioneering work of Quirk and Schofield (1955), which is very close to the rK_{sat}=50% at C_{TH} recommended by Shainberg and Letey (1984) and similarly very close to irreparable damage to the soil resource. The current work demonstrates the soil-specific nature of the C_{TH}, and similarly we should expect the C_{TU} to be soil-specific with potential to occur at rK_{sat}<50%. There appears to be very little information on the rK_{sat} associated with the C_{TU} indicating further investigation is required (Dang et al. 2018). Hence, where the rK_{sat} associated with the C_{TH} is to be increased for practical irrigation reasons, it needs to be done where the C_{TU} is known and some level of safety factor has been applied.

3.7 Conclusion

The semi-empirical approach to C_{TH} determination used in the disaggregation model of Ezlit et al. (2013) was validated against seven soils where MQSS water had been used for irrigation of soil under field conditions. This indicates that C_{TH} determination via the disaggregation model will allow proactive planning of irrigation systems with regard to water quality and is a good measure for identification of MQSS water as a strategic resource. The C_{TH} was further supported as being soil-specific, even within soil classification, demonstrating that it is important to move on from generalised guidelines for water quality in agricultural production. Discussion was subsequently presented to aid in the development of such guidelines and for the increase of saturated hydraulic reduction that is considered tolerable.

3.8 Acknowledgements

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4 Evaluating dispersive potential to identify the threshold electrolyte concentration in non-dispersive soils

Dang, A.[1], Bennett, J. McL.[1], Marchuk, A.[1], Biggs, A.[2], and Raine, S.R.[1]*

[1] *University of Southern Queensland, West St, Toowoomba, QLD 4350, Australia*

[2] *Department of Natural Resources and Mines, Tor St, Toowoomba, QLD 4350, Australia*

[*] *Corresponding authour: John.Bennett@USQ.edu.au*

4.1 Abstract

Use of non-traditional and marginal quality saline sodic water will increase in water limited environments and methods to assess use suitability are required. The threshold electrolyte concentration (C_{TH}) defines the acceptable reduction in soil hydraulic conductivity for a given solution sodicity maintained at the C_{TH}. The traditional method of determining C_{TH} is via leaching columns, which is laborious and often expensive. Dispersive potential P_{DIS} is potentially a more rapid method via which to determine the C_{TH} in a practical sense and make management recommendations for water quality use on a given soil. This work evaluates the P_{DIS} method against known C_{TH} data to determine the efficacy of use for non-dispersive soils irrigated with marginal quality saline sodic water. Results suggest that the P_{DIS} approach to C_{TH} did not reliably, or efficiently, determine the C_{TH} in non-dispersive soils equilibrated with an irrigation solution. Using it to determine the aggregation and dispersion boundary for initially non-dispersive soil appeared to be meritorious, but only where the aggregates equilibrated with the irrigation solution were subject to rapid dilution with deionised water.

4.2 Introduction

Traditional agricultural good quality water resources are insufficient given the increasing and competing industrial demand on the finite resource (Dubois 2011). Due to this pressure, there is case to utilise non-traditional, marginal quality saline-sodic (MQSS) water — containing sodium adsorption ratio (SAR) and salinity beyond traditional recommendations ((ANZECC 2000)) — as a resource. However, if not used strategically, such water can degrade soil structure stability and hamper crop production (Bennett & Warren 2015; Oster 1994; So & Aylmore 1993). Hence, an understanding of inherent soil structural response is crucial in determining the strategic

use of MQSS water. The loss in porosity, decreased infiltration and reduced crop productivity associated with irrigation via sodic water (Oster & Schroer 1979; So & Aylmore 1993) is a function of the water quality as well as the physical factors of the soil. Increased soil solution salinity (i.e. lower osmotic potential in the bulk soil solution) results in a compressed diffuse double layer (DDL) and increased soil stability (Quirk & Schofield 1955). The threshold electrolyte concentration (C_{TH}) is determined as a 20% reduction in soil hydraulic conductivity (de Menezes et al. 2014; Ezlit et al. 2013), which represents an arbitrary, but measureable, departure from the soil stable condition due to volume change in the clay domain (swelling and disaggregation) (Quirk 2001). Importantly, the C_{TH} is known to be soil specific and currently requires a semi-empirical approach to determination (Bennett & Raine 2012; Ezlit et al. 2013) that is highly laborious (2–3 weeks depending on the soil), resulting in associated measurement costs that could be prohibitive to agricultural routine use. Hence, there is requirement to investigate the efficacy of other methods to determine this factor rapidly.

Dispersive potential (P_{DIS}) (Rengasamy & Olsson 1991) is designed as an alternative to the C_{TH} approach (Ezlit et al. 2013) in determining the suitability of a MQSS for irrigation, based on the difference between the osmotic pressure at the threshold concentration (P_{TEC}) and the pressure in the soil solution concentration to achieve complete flocculation (P_{SOL}) (Marchuk & Rengasamy 2012; Rengasamy & Sumner 1998). Dispersive potential is designed to eliminate the soil-specific variation in determining the threshold point.

$$P_{DIS} = P_{TEC} - P_{SOL}, \quad \text{for} \quad P_{SOL} < P_{TEC} \qquad \text{Equation 4.1}$$

The P_{DIS} term includes the flocculating power of the individual cations (Rengasamy, 2002) in the calculation of P_{TEC}, defined as:

$$P_{TEC} = 3.6 \times \left(45[C_{Ca}] + 27\left[C_{Mg}\right] + 1.8[C_K] + [C_{Na}]\right) \qquad \text{Equation 4.2}$$

Where square parentheses indicate the soluble cation concentration at the threshold electrolyte point in $mmol_c/L$ and 3.6 represents the osmotic pressure in kPa per mol_c m^3.

The purpose of the P_{DIS} approach is to provide a unifying concept that rapidly determines the tendency of clay particles to disperse and provide information on a soil-

specific basis. It achieves soil specificity through empirical measurement to eliminate the requirement for prediction of soil-specific response variables, thus facilitating more specific management advice. However, dispersive potential actually calculates the turbidity concentration (C_{TU}) (Quirk & Schofield 1955). The C_{TU} refers to the point at which dispersed clay particles start to appear in the percolating solution and the concentration of the solution is at about ¼ of the C_{TH} (Quirk 2001), therefore, the P_{DIS} approach may have limitations in this sense. Furthermore, while P_{DIS} concept utility has been for examined for existing dispersive soils, or soils made to be dispersive and subject to rapid dilution with distilled water to simulate 'rainfall' (Marchuk & Rengasamy 2012; Rengasamy & Olsson 1991). The practicality of the method to determine an irrigation water quality suitability to a non-dispersive soil has not been tested in equilibration with the irrigation solution. Therefore, the aim of this study is to investigate the capability of dispersive potential to determine soil-specific C_{TH} in non-dispersive Vertosols irrigated with MQSS.

4.3 Materials and Method

This work seeks to determine if P_{DIS} is an efficient method for determining C_{TH}. In testing this, the work assumes that P_{TEC} is equivalent to the pressure at the C_{TU} ($P_{C_{TU}}$), and that C_{TU}x4=C_{TH} for the given SAR (Quirk & Schofield 1955); the latter is an approximation, but would provide a means by which to apply a practical safety measure for soils in the identification of C_{TH}. Therefore, the following equations define P_{DIS}:

$$P_{DIS} = P_{C_{TU}} - P_{SOL}, \quad \text{for} \quad P_{SOL} < P_{C_{TU}} \qquad \text{Equation 4.3}$$

$$P_{C_{TU}} = 3.6 \times \left(45[C_{Ca}] + 27\left[C_{Mg}\right] + 1.8[C_K] + [C_{Na}]\right) \qquad \text{Equation 4.4}$$

$$P_{SOL} = 3.6 \times \left(45[C_{Ca}] + 27\left[C_{Mg}\right] + 1.8[C_K] + [C_{Na}]\right) \qquad \text{Equation 4.5}$$

where square parentheses indicate the soluble cation concentration in $mmol_c/L$ measured at either point, and 3.6 represents the osmotic pressure in kPa per mol_c m^3. The initial methodology for this method was provided in Rengasamy (2002). It was noted that obtaining results for an initially non-dispersive Vertisol subject to MQSS was much more subjective than for a soil that was spontaneously dispersive; without the direct use of a turbidimeter. Therefore, it was hypothesised that the observational

method could be misleading. Hence, the titration method provided in (Marchuk & Rengasamy 2012) was also investigated.

4.3.1 Initial properties of the soils

Five Vertisol soils (IUSS Working Group 2014), of different clay mineralogy, clay content, EC, pH (Table 4.1) were used in this study and collected from cotton farms in southeast Queensland. Soil samples were collected uniformly from a 0–0.2 m depth, air-dried, and gently ground to pass a 2 mm sieve.

Soil pH and electrical conductivity (EC) were determined in a single 1:5 soil: de-ionised (DI) water sample using a Radiometer analytical ION 450 Meter. Exchangeable cations were determined using a Perkin Elmer NexIon-ICP MS (Inductively Coupled Plasma – Mass Spectrometer). For exchangeable cations, the samples were extracted with 0.5 M NH_4Cl pH adjusted to 7.2 or 8.2 to match the pH of the soil analysed (Marchuk & Rengasamy 2012). The exchangeable cations were put through a centrifuge for 15 mins, and analysed on the ICP-MS to calculate ESP and EDP (See: Rayment and Lyons, 2011 – method 15A2).

Net negative charge, measured as the electrophoretic mobility of clay particles (zeta potential; ζ), provides a measure of the actual charge available for hydration interactions. The tendency of clay colloids to disperse can be assessed by use of the zeta potential (ζ) obtained from electrophoresis experiments (Aydin et al. 2004). Zeta potential of the samples was measured using a Malvern Zetasizer (See: Marchuk and Rengasamy 2012). Briefly, 1:5 soil:DI water suspensions were prepared and upended carefully three times (spontaneous dispersion), or shaken by upending 20 times (mechanical dispersion), and then left to sit for 4 hours before extraction.

Spontaneous dispersion samples were then analysed on the Malvern Zetasizer, while both spontaneous and mechanical dispersion were measured for turbidity (NTU) using a NACH 2100N turbiditimeter. Soil soluble and exchangeable cations (Rayment & Lyons 2011), turbidity, clay content, water dispersible clay, and zeta potential of the dispersed clays are presented in Table 4.1

Table 4.1. Selected physico-chemical properties of five surface soils (0-10 cm soil depth) collected from cotton farms in southeast Queensland

	Units	*Soil 1* Mungana	*Soil 2* Yarrandoo	*Soil 3* Corinda	*Soil 4* Dunholm	*Soil 5* Maclands
Location		-27.022, 151.126	-27.23, 151.32	-27.037, 151.125	-27.077, 151.134	-27.020, 151.167
pH		8.6	7.2	7.8	8.0	7.27
EC	dS/m	0.1	0.21	0.13	0.05	0.19
Soluble Cations (mmol$_c$/L)	Na	0.86	0.77	0.09	0.059	1.87
	Mg	0.63	0.52	0.14	0.08	0.27
	K	0.09	0.1	0.01	0.019	0.10
	Ca	1.03	0.76	0.06	0.204	0.45
TCC	mmol$_c$/L	2.61	2.16	0.31	0.36	2.69
Exchangeable Cations (meq/100g)	Na	0.4	0.39	1.03	0.94	3.73
	Mg	8.67	2.87	14.81	10.66	14.52
	K	2.95	0.66	0.96	0.69	1.12
	Ca	25.52	11.66	24.3	14.09	19.87
SAR		0.98	0.96	0.29	0.157	0.19
CROSS		1.13	1.12	0.37	0.22	0.44
ESP	%	1.07	2.5	2.5	3.55	9.51
EDP	%	6.30	5.53	5.14	6.51	12.47
CEC	meq/100g	37.5	15.6	41.1	26.4	39.24
Soil Texture	Australian classification	Clay	Clay	Clay	Clay	Clay
Clay content	%	75	52	61	60	62
Water-dispersible clay	%	53	35	56	52	35
Zeta potential	mV	-22.8	-23	-27	-29	-16
Organic Carbon	%	1.06	1.01	1.02	0.98	1.31
Dispersion as turbidity (NTU)	Spontaneous	650	200	650	124	118
	Mechanical	2050	850	2050	1566	1566

EC, electrical conductivity (dS/m); TCC, total cation concentration (mmol$_c$/L); SAR, sodium absorption ratio; CROSS, cation ratio of soil structural stability; ESP, exchangeable sodium percentage; ECR, exchangeable cation ratio (%); CEC, cation exchange capacity (meq/100g).

The initial properties of the soils were quite similar, Soil pH ranged between 7 and 8.6. The soil SAR was <1 and the soil EDP (Bennett et al., 2016) was <5 for all soils. While all the soils were clay soils with clay content generally ranging between 60–75%, Soil 2 had a lower clay content of 50%. Each of the soils before treatment with MQSS water, had zeta potential <30 mV indicating that these soils were non-dispersive, which was supported by results for spontaneous dispersion.

4.3.1.1 *X-Ray diffraction (XRD) analysis*

Substantial differences in C_{TH} curve dimensions have been identified between different soil types, due to variations in mineralogy (Churchman & Oades 1995), clay content (Frenkel et al. 1978; Goldberg et al. 1991; McNeal & Coleman 1966) and organic matter type and content (Nelson & Oades 1998). The type and amount of clay mineral in soil is thought to be the dominating factor relating to soil dispersion/flocculation and reduction in hydraulic conductivity (Ezlit et al. 2013; Goldberg et al. 1991). Soil clay mineralogy can significantly affect a number of soil physical and chemical properties (Marchuk et al. 2013a).

In order to improve the identification of the mineralogical composition of the soils by XRD analysis, clay fractions were separated by sedimentation (Jackson 2005). No addition of dispersing agents or chemical treatments (such as for organic matter or oxide removal) were made to the clay samples. Dry clay samples were finely ground (<2 μm fraction) and backfilled into steel holders for XRD analysis. The XRD patterns for randomly oriented air-dried samples were recorded with a PANalytical X'Pert Pro Multi-purpose diffractometer using Fe filtered CoKα radiation, automatic divergence slit, 2° anti-scatter slit and fast X'Celerator Si strip detector. The diffraction patterns were recorded from 3 to 80° 2θ with a 0.5 second counting time per step for an overall counting time of approximately 30 minutes.

Interpretation of data was also consistent with Marchuk (2016) using CSIRO software XPLOT for Windows (Raven 1990) comparing the XRD patterns with the International Centre for Diffraction Data (ICDD) database of standard diffraction patterns using computer aided search/match algorithms. The quantitative estimation of clay phases for all 5 soils are presented in Table 4.2. All soils were Montmorillonite dominant, except Soil 2 (Quartz dominant).

Table 4.2. Mineralogical composition of clays (%) from XRD analysis

Soil	*Montmorillonite*	*Kaolinite*	*Anatase*	*Hematite*	*Quartz*
Mungana	76	10	4	1	9
Yarrandoo	23	21	4		52
Dunholm	72	7	3	1	17
Corinda	62	6	3		29
Maclands	60	7	4	1	28

4.3.2 Methodology to determine Dispersive potential

The method used to determine dispersive potential was a modification of the clay dispersion method, described by Rengasamy (2002). The original method was designed to measure dispersion for an already dispersive soil. Furthermore, the original method utilised deionised water to undertake all measurements, which was assumed to simulate a rainfall environment, and not an environment where poor quality irrigation water is used. Hence, modification of the method included: 1) equilibration of the soil sample to a given MQSS water; and 2) undertaking all measurements within this water quality. These modifications allowed assessment of the expected water quality effect on the soil in determining C_{TU}, rather than the dispersion point of an already dispersive soil.

Figure 4.1 depicts the experimental concept, which is based on Rengasamy (2002). For any soil there is a C_{TU} that will exist in a matrix of SAR and EC (the solid line). It is assumed that above the solid line (threshold) combinations of EC and SAR will cause a soil to disperse while below the line it will remain aggregated. The aim of a simple method is to predict the solid line. Therefore, by choosing a set of reasonable SAR and EC values the threshold concentration at any of the treatment SARs should be encompassed by the EC treatments, allowing a sequential EC bracketing approach to determination of the threshold EC (crosses) at the given SAR. The C_{TU} value determined by observation, can then be used to theoretically calculate the C_{TH}.

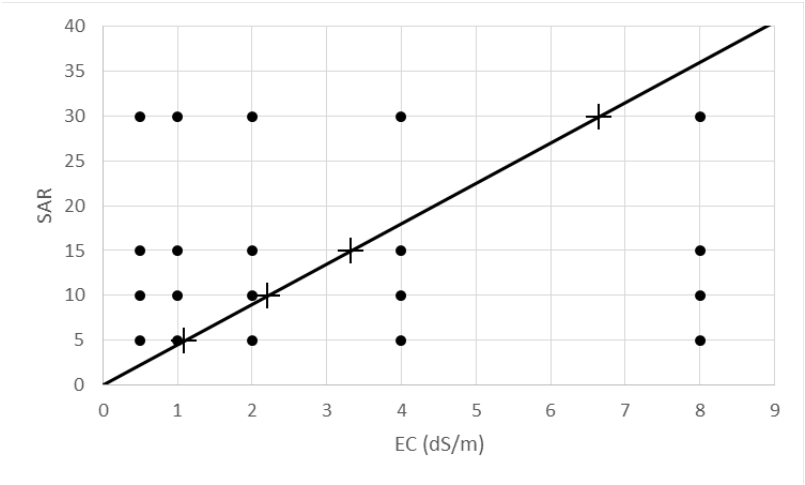

Figure 4.1 Experimental conceptualisation: Dots represent the actual solution concentrations used in the approach, while the solid line is a theoretical representation of the possible C_{TH} (solid line) the approach is designed to predict. The crosses represent the point that each sodium adsorption ratio (SAR) treatment is required to predict, which will sit between salinity and SAR values as described by Rengasamy (2002).

4.3.2.1 *Equilibration with irrigation solution*

Following the method of Bennett and Raine (2012), soil columns for all five soils were prepared for subsequent treatment, in line with Table 4.3, using 87.5 mm internal diameter, 100 mm polyvinylchloride pipe; there were 250 columns prepared in total. One end of each column was closed at the bottom using plastic mesh onto which a trimmed filter paper (Whatman grade 1) was placed internally. Each soil was ground to pass a 2 mm sieve. Then 400 g of the respective soil was transferred into the respective column; to achieve uniform density this was done in 2x25 mm lifts to create the 50 mm soil column, with gentle pressure applied to each lift to ensure the correct mass per volume. Another filter paper was placed on the top of each soil column to avoid soil disturbance when adding irrigation solutions. Two replicates were used for each treatment. Prior to experimental equilibration, columns were saturated overnight from the base of the column using a 0 mm head, immersed in their respective treatment solution.

Soil columns were equilibrated with irrigation solution using a saturated hydraulic conductivity (K_{sat}) leaching approach with a hydraulic head of 10 mm (Klute 1965). All cores were run until a steady state hydraulic conductivity was reached, at which time equilibration was assumed to have occurred; for all soils equilibration was observed within seven pore volumes. Reduction in hydraulic conductivity from the stable state (rK_{sat}) was recorded during this time. We defined steady state based on volume measurements i.e. less than 3% variation in the volume between consecutive measurements after a 10 min interval for at least 1h (Reading et al. 2015). This process was undertaken for all 25 salt concentrations combinations of SAR (5–30) and EC (0.5–8.0 dS/m) comprised of NaCl and $CaCl_2$ salts (Table 4.3). A simplified Na and Ca system was used in this experiment as K and Mg effects on soil structure are shown to be optimisable, meaning that their effect is soil-specific (Smith et al. 2015) and therefore would potentially confound the basis of the comparative experiment. Leachate was collected in plastic containers at the bottom of the column.

Following equilibration, soils were removed from the polyvinylchloride columns. They were then dried at 40˚C and carefully ground to pass through <2mm sieve for the measurement of ζ potential, Exchangeable Sodium Percentage (ESP), and Turbidity.

Table 4.3. Concentration of sodium and calcium (g/L) required to make each SAR solution (0, 5, 10, 15, and 30) at the assigned EC (0.5, 1, 2, 4, and 8 dS/m)

Treatment	SAR 5		SAR 10		SAR 15		SAR 30	
EC (dS/m)	Na (g/L)	Ca (g/L)	Na (g/L)	Ca (g/L)	Na (g/L)	Ca (g/L)	Na (g/L)	Ca (g/L)
0.5	0.224	0.086	0.268	0.031	0.280	0.015	0.289	0.004
1.0	0.383	0.253	0.499	0.107	0.540	0.056	0.572	0.016
2.0	0.628	0.681	0.895	0.345	1.013	0.196	1.121	0.060
4.0	0.992	1.695	1.533	1.013	1.829	0.641	2.160	0.223
8.0	1.519	3.976	2.513	2.723	3.158	1.911	4.051	0.786

4.3.2.2 *Observational dispersive potential method*

This approach is that of Rengasamy (2002) modified as suggested above. An air dried soil sample of 10 g was obtained from each treatment and soil replicate, following leaching with the different SAR-EC treatments, and was placed into a 150 mL sample jar. Then 100 mL of the respective SAR-EC combination solution was added. The jars were upended carefully three times, and then allowed to settle for prior to measurement of dispersion/flocculation. The amount of dispersion/flocculation present in each jar was analysed visually (binary – present, or not-present) after 16 h and using a HACH 2100N turbiditimeter after 4, 8, 12, and 16 h. At this juncture it was found that all soils flocculated, even under high SAR and low EC treatments (Table 4.4); the method was further adjusted to investigate the practicality of the method.

As per Marchuk and Rengasamy (2012) the equilibrated irrigated soils were subject to DI water. The irrigation solution was carefully decanted so as not to lose any soil aggregates. The volume was replaced with DI, and the above process repeated in accordance with Rengasamy (2002). The EC and SAR of the new solution contained in each jar was determined. The jar with the lowest EC at which complete flocculation occurred was selected. The C_{TU} occurs between the EC of the selected complete flocculation jar and the EC of the sequential dispersed jar preceding it. As the C_{TU} point sits between these two EC values, five new solutions at a constant SAR value (varied across soils and which value was being analysed) but with range of EC between the dispersion-flocculation EC values (this varied between soils) were prepared. This process was repeated until the difference between the dispersion and flocculation EC was <0.1 $mmol_c/L$. Once this point was reached this EC value was assumed to be the

C_{TU}. The EC and SAR of the samples chosen as the C_{TU} point were remeasured using a 30 mL sample of solution. These values were used to calculate the dispersive potential.

4.3.2.3 *Titration dispersive potential method*

This approach is similar to that of Marchuk and Rengasamy (2012), which allows for equilibration of the solution and soil, but then disperses this with DI water and titrates back to flocculation. Concurrent to the observational method, another set of air-dried soil samples (10 g each) was weighed into 150 mL sample jar, and 100 mL of the respective SAR-EC solution combination was carefully added into the jars. The jars were mechanically shaken end-over-end 20 times and left to sit for 12 hours. Then 30 mL of turbid suspension was removed from each jar and placed into a 50 mL falcon tube. The turbid solutions were then allowed to settle for 72 h to allow for complete flocculation where possible. Samples that remained turbid were subsequently titrated with NaCl-$CaCl_2$ solution (concentration and ratio dependent on the respective treatment SAR and EC), sufficient to achieve a 0.1 dS/m increase within the falcon tube, every 12 hours. Titration continued until the falcon tube solution was visually at a point of complete flocculation. The EC and SAR of the sample was again measured again to determine C_{TU}.

4.3.3 Threshold determination in rapidly diluted samples

Given the result of generally unstable clay suspension when measurements were taken in the MQSS equilibrium solution, we sought to rapidly dilute the sample to induce dispersion. The logic of this approach was that: 1) for soils where dilution decreased osmotic compression of the diffuse double layer controlling stability, these soils would disperse; and 2) where change in the osmotic pressure was not important to soil stability at the given solution concentration, dispersion would not occur providing a means to measure to measure C_{TU} (Oster & Grattan 2002; Oster et al. 2012; Quirk & Aylmore 1960). From this the C_{TU} was directly measured and the C_{TH} calculated based on Quirk and Schofield's (1955) observation that the C_{TH} occurred at solution concentration effectively one quarter that at the C_{TU}.

4.3.4 Statistical analyses

From both the observational and titration obtained datasets, the C_{TU} points were graphed (SAR-EC) and a linear regression line was fitted using a calculated Pearson's

product-moment correlation coefficient. Direct comparison of these linear regressions were subsequently undertaken.

4.4 Results

4.4.1 Solution induced reduction in hydraulic conductivity

During the equilibration process of the soil cores to each respective solution the rK_{sat} values were recorded with reference to a $CaCl_2$ benchmark solution hydraulic conductivity, prepared at the intended EC for the respective core (SAR=0). Table 4.4 shows rK_{sat} as a percentage reduction from this benchmark and demonstrates that all soils incurred a reduction of ≈90% at some point in the treatment process, but usually at SAR=30 and EC=0.5 dS/m. The extent of hydraulic reduction at a given SAR was reduced by an increase in EC, which was expected, for all soils and SAR treatments.

Table 4.4. Percent reduction in saturated hydraulic conductivity based on sodium adsorption ratio (SAR) and electrical conductivity (EC) of the percolating solution.

EC (dS/m)	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
			SAR 5		
0.5	42.1	50.2	60.0	46.4	42.3
1	18.8	18.1	53.1	31.0	20.3
2	6.2	4.1	45.6	18.0	11.7
4	1.6	2.8	37.3	8.9	2.2
8	0.3	0.1	28.1	3.5	0.5
			SAR 10		
0.5	73.0	76.7	70.2	73.5	68.4
1	47.5	43.2	63.1	58.2	43.8
2	21.7	13.5	54.9	39.7	29.2
4	6.8	8.3	45.2	22.0	6.9
8	1.4	0.3	33.8	9.1	1.6
			SAR 15		
0.5	78.4	90.9	77.4	76.8	84.8
1	62.0	70.6	70.8	66.3	67.0
2	44.4	33.9	62.5	59.6	52.0
4	17.7	2.5	52.2	38.0	16.7
8	4.2	1.1	39.3	17.2	4.3
			SAR 30		
0.5	88.9	99.5	90.3	87.9	98.5
1	86.6	98.2	86.0	85.6	95.9
2	79.7	92.6	79.8	80.3	92.6
4	69.6	70.8	70.4	78.2	69.0
8	30.8	24.8	56.1	52.6	32.7

4.4.2 Dispersive potential in marginal quality irrigation solution

Assessing dispersed clay in suspension where the measurement was taken within the marginal quality irrigation solution generally yielded a flocculated result (NTU<99) for all solutions (Table 4.5). Soil 2 and Soil 5 provided exception to this for the SAR=30 and EC=0.5 dS/m solution, where the turbidity in solution indicated a low–medium-low turbidity; for Soil 2 the SAR=30 EC=10, 15 dS/m also indicated low turbidity. This equated to <0.1% of clay remaining in suspension after 16 h for Soils 1, 3 and 4, while Soil 2 had 0.30 and Soil 5 had 0.18% dispersed clay remaining in suspension after 16 h.

Table 4.5. Turbidity (Turb; NTU) and dispersed clay percentage (Zhu et al., 2016) for soils equilibrated with marginal quality irrigation solution and measured in that same solution after 16 hours (h).

EC (dS/m)	*Soil 1*		*Soil 2*		*Soil 3*		*Soil 4*		*Soil 5*	
	Turb	*Clay (%)*	*Turb*	*Clay (%)*	*Turb*	*Clay (%)*	*Turb*	*Clay (%)*	*Turb*	*Clay (%)*
					SAR 5					
0.5	47	0.032	161	0.109	170	0.115	40	0.027	37	0.025
1.0	40	0.027	38	0.025	45	0.030	12	0.008	27	0.018
2.0	26	0.018	26	0.017	52	0.035	15	0.010	26	0.018
4.0	25	0.017	20	0.013	35	0.024	6	0.004	29	0.019
8.0	30	0.020	18	0.012	35	0.024	9	0.006	15	0.010
					SAR 10					
0.5	67	0.045	248	0.168	363	0.246	74	0.050	234	0.159
1.0	41	0.027	132	0.089	70	0.047	16	0.011	38	0.026
2.0	23	0.016	26	0.018	45	0.031	6	0.004	28	0.019
4.0	17	0.011	29	0.020	39	0.027	5	0.004	21	0.014
8.0	18	0.012	16	0.011	31	0.021	7	0.005	21	0.014
					SAR 15					
0.5	32	0.022	441	0.299	444	0.301	111	0.075	247	0.167
1.0	22	0.015	275	0.186	107	0.072	25	0.017	57	0.039
2.0	14	0.010	52	0.035	44	0.029	13	0.009	26	0.017
4.0	21	0.014	17	0.011	40	0.027	9	0.006	25	0.017
8.0	26	0.017	11	0.008	28	0.019	10	0.007	14	0.009
					SAR 30					
0.5	40	0.027	444	0.301	591	0.400	99	0.067	268	0.181
1.0	18	0.012	414	0.280	126	0.086	35	0.024	59	0.040
2.0	18	0.012	290	0.196	69	0.047	18	0.012	46	0.031
4.0	22	0.015	49	0.033	32	0.022	15	0.010	26	0.018
8.0	42	0.028	16	0.011	31	0.021	13	0.009	25	0.017
Max	*67*	*0.045*	*444*	*0.301*	*591*	*0.400*	*111*	*0.075*	*268*	*0.181*

4.4.3 Dispersive potential in deionised water

Where the soil samples equilibrated with the various marginal quality irrigation water treatments were subject to rapid dilution with deionised water (pH 7, EC $7x10^{-4}$ dS/m) the turbidity, and subsequent percentage of dispersed clay, significantly increased at EC=0.5 and 1.0 dS/m for all SAR treatments, EC=2.0 dS/m for SAR>10 treatments, and EC=4.0 dS/m for SAR>15 treatments (p<0.05). Where significant increase in turbidity was observed this resulted in medium to very-high turbidity (1000–3000NTU) (Zhu et al. 2016), with dispersed clay ≥1.4% (very high - >3000NTU) where EC=0.5 dS/m and SAR=30 treatment solutions had been applied.

Table 4.6. Turbidity (Turb; NTU) and dispersed clay percentage (Zhu et al., 2016) for soils equilibrated with marginal quality irrigation solution and measured in deionised water after 16 hours (h).

EC (dS/m)	Soil 1		Soil 2		Soil 3		Soil 4		Soil 5	
	Turb	Clay (%)	Turb	Clay (%)	Turb	Clay (%)	Turb	Clay (%)	Turb	Clay (%)
					SAR 5					
0.5	2280	1.544	661	0.447	3126	2.116	2027	1.372	1269	0.859
1	2958	2.003	553	0.374	2925	1.980	2442	1.653	1473	0.997
2	73	0.050	448	0.303	67	0.045	836	0.566	346	0.234
4	26	0.018	54	0.037	13	0.009	62.3	0.042	15	0.010
8	8	0.005	12	0.008	13	0.009	12	0.008	18	0.012
					SAR 10					
0.5	2675	1.811	1661	1.124	3133	2.121	2636	1.785	2241	1.517
1	2038	1.380	1048	0.709	2865	1.940	4178	2.829	1572	1.064
2	1744	1.181	889	0.602	1952	1.322	3269	2.213	1495	1.012
4	38	0.026	311	0.211	47	0.032	37	0.025	1149	0.778
8	4	0.002	15	0.010	11	0.008	27	0.018	24	0.016
					SAR 15					
0.5	2766	1.873	1302	0.881	1926	1.304	4267	2.889	1407	0.953
1	2096	1.419	1156	0.783	1956	1.324	3588	2.429	1184	0.802
2	1369	0.927	716	0.485	1424	0.964	2151	1.456	997	0.675
4	627	0.424	496	0.336	179	0.121	1655	1.120	298	0.202
8	53	0.036	33	0.022	69	0.047	11	0.007	27	0.018
					SAR 30					
0.5	4770	3.229	2073	1.403	2428	1.644	4095	2.772	2603	1.762
1	3930	2.661	2290	1.550	2596	1.757	3925	2.657	2509	1.699
2	2970	2.011	1428	0.967	1902	1.288	2789	1.888	2069	1.401
4	1748	1.183	1351	0.915	1912	1.294	1941	1.314	1633	1.106
8	73	0.05	470	0.318	22	0.015	97	0.066	1974	1.336
Max	*4770*	*3.229*	*2290*	*1.550*	*3133*	*2.121*	*4267*	*2.889*	*2603*	*1.762*

The C_{TU} functions obtained by either the observational or titration method were in reasonable agreement (Figure 4.2). It was generally the case that the titration method provided a lower threshold EC for the same SAR as compared to the observational method. The C_{TU} relationship had very good fit irrespective of the method used with R^2>0.87, indicating that at least 87 percent of the variation was explained for all soils. Significant differences between the C_{TU} lines were observed for the different soils, depending on the method used. Using the titration method, there was no significant difference between Soil A and Soil C. Soils B, D and E, were all statistically similar (p<0.05). However, using the observational method, Soil A was significantly different to all other soils, while all other soils were statistically similar.

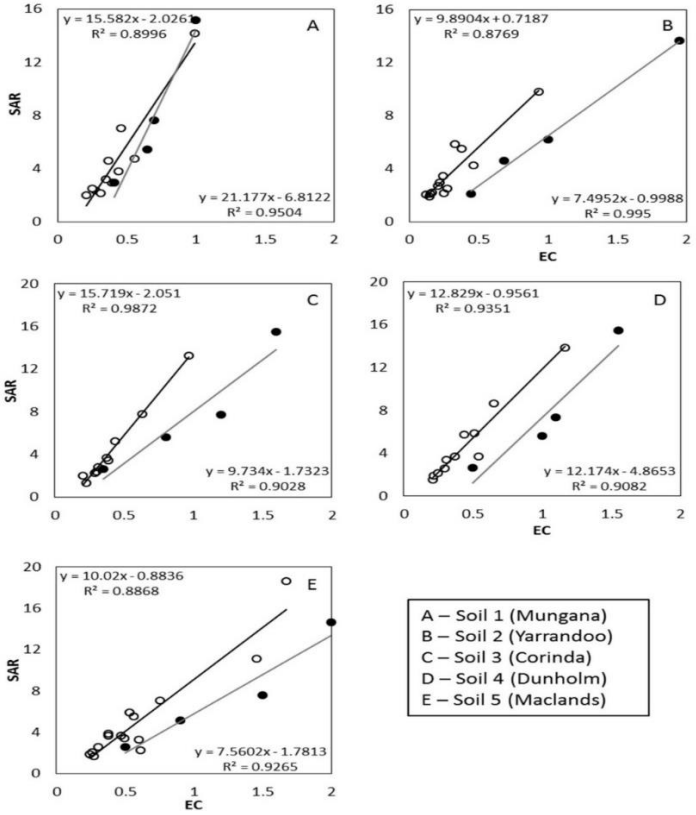

Figure 4.2. Turbidity concentration thresholds as determined by the dispersive potential approach in a deionised water environment by observational (● – Grey trend-line) and titration (○ – black trend-line) methods. The trend line equation and R^2 in the top left pertains to titration, while that in the lower right pertains to observational results. The trend line equation and R^2 in the top left pertains to titration, while that in the lower right pertains to observational results. The standard error of the regression was <1.0 for all soils except for E, where the standard error was <2.0 (standard error in units of SAR).

4.4.4 Threshold electrolyte concentration calculation

In this work it is assumed that P_{TEC}=C_{TU} and that C_{TU}/4=C_{TH} for the given SAR (Quirk & Schofield 1955). Using this approach, the hashed line in Figure 4.3 represents the

calculated C_{TH} which is simply the solution concentration at the C_{TU} divided by 4, and represents a 10% rK_{sat}. As shown in Figure 4.3, For Soil 1 the calculated C_{TH} appears to fit the rK_{sat} data very well, with all observed data for rK_{sat}<10% below the C_{TH} line. The placing of the two different data sets (Filled circles (●) represent solutions where a reduction in hydraulic conductivity was observed as <10% (Table 4.6), while unfilled circles (○) represent experimental solutions where reduction in hydraulic conductivity was observed as ≥10%) shows that the calculated C_{TH} appears to fit the rK_{sat} data. However, for all other soils at least one of the experimental solution observations does not fit the C_{TH} equation. For Soil 2 and 5, the data point on the dispersive side of the C_{TH} line is potentially within the margin of error (unknown due to the line being a calculation). Soil 3 suggests that the calculated C_{TH} is not suitable for interpreting the observed results, where all solutions applied cause rK_{sat}>10%.

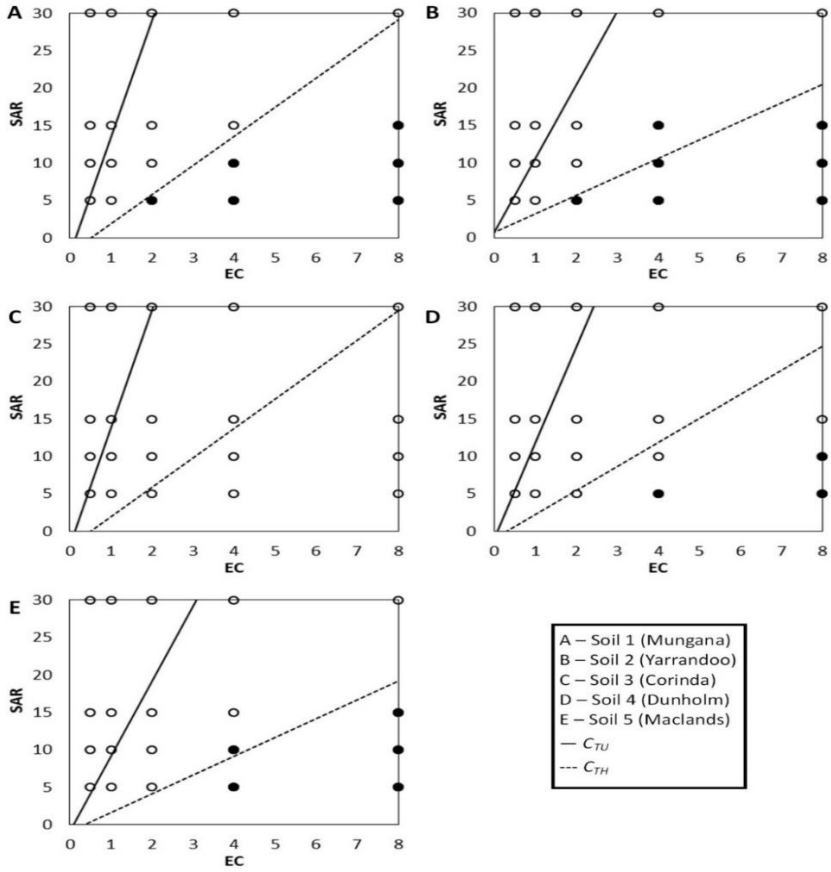

Figure 4.3. Experimental solution concentrations for the five soils (represented as circles) plotted against the threshold turbidity concentration (C_{TU}) and the calculated threshold electrolyte concentration (C_{TH}), which represents a 10% reduction in hydraulic conductivity. Solution concentration below the C_{TH} line are assumed maintain the soil in a stable state, while those above cause dispersion. Filled circles (●) represent solutions where a reduction in hydraulic conductivity was observed as <10% (Table 4.4), while unfilled circles (○) represent experimental solutions where reduction in hydraulic conductivity was observed as ≥10%

4.5 Discussion

4.5.1 Dispersive potential for assessment of marginal quality water effect on non-dispersive soils

This study aimed to investigate the capability of dispersive potential to determine soil-specific C_{TH} in non-dispersive Vertisols irrigated with MQSS. Results for turbidity measured in the MQSS solute matrix (T) suggest that the P_{DIS} method is not useful when turbidity data is considered in isolation; i.e. to achieve a turbidity value that begins to correspond with the rK_{sat} observed (Table 4.4) samples were required to undergo rapid dilution with DI water, as per the initial approach of Marchuk and Rengasamy (2012). However, when considering the MQSS turbidity and associated rK_{sat} together, an interesting result is observed (Figure 4.4).

The turbidity threshold for a stable aggregate is documented at 100 NTU (Zhu et al. 2016), while (Quirk & Schofield 1955) demonstrated that a significant reduction in saturated hydraulic conductivity occurred prior to clay particles appearing in the leachate, and this threshold can be calculated at 56% rK_{sat}; Quadrant A, of Figure 4.4, occurs beneath the intersection of these thresholds. While we acknowledge that the threshold of Quirk and Schofield (1955) is likely to vary from soil to soil (Ezlit et al. 2013; McNeal & Coleman 1966; Quirk 2001), this threshold makes for important discussion when keeping this in mind. We suggest that the data within Quadrant A is hydraulic reduction due to expansion of the clay domain as explained by Quirk and Schofield (1955) and Quirk (2001), which is the combination of swelling within the clay-quasicrystal and disaggregation, due to diffuse double layer development prior to dispersion.

Data to the right of the turbidity stable aggregate threshold (NTU=100) suggests that dispersion has occurred and that aggregates are now inherently unstable (Quadrant C; Figure 4.4). The fitted linear regression line was significant ($p<0.01$) and represents 33% of the observed variance; an increase in turbidity (dispersed clay) associated with greater percent rK_{sat} is something that we would expect (McNeal & Coleman 1966; Oster & Schroer 1979). There are two data points in Quadrant D, which we believe is simply an artefact of dispersion/flocculation boundary as represented by a 56% rK_{sat} being variable between soils. In fact, Quadrant D should devoid of data for a given soil on the logic of a soil sample remaining stable also not crossing the stable NTU boundary. Therefore, we would consider the data in Quadrant D to be a part of

Quadrant C and that this quadrant represents the point where diffuse double layer development causes clay domain volume change in excess of attractive forces (primarily van der Waals forces).

It is Quadrant B that provides concern over the use of P_{DIS} in defining the C_{TU} and then calculating C_{TH} from this. Approximately one third of the data resides in this region where rK_{sat}>> than the threshold in the work of Quirk and Schofield (1955), but turbidity responses represented a stable soil (NTU<100). It is possible that the rK_{sat} boundary for individual soils is greater than that in Quirk and Schofield (1955), but this requires more detailed investigation to speculate about values of 90% rK_{sat} and apparently no spontaneous dispersion. At this juncture it is also worth considering that the soils with NTU>100 all had NTU much less than might have been expected, with dispersed clay<0.4% for all soils, which was confirmed when these same soils were rapidly diluted with DI water and turbidity subsequently tested (Table 4.6). There is need to provide greater understanding of the extent of dispersion under the osmotic pressure of MQSS solutions of concentration that should induce spontaneous dispersion. Based on this, we do not consider the use of P_{DIS} as advisable for determination of C_{TH} where the soil was initially non-dispersive and measured at equilibrium in the equilibrium solution (MQSS).

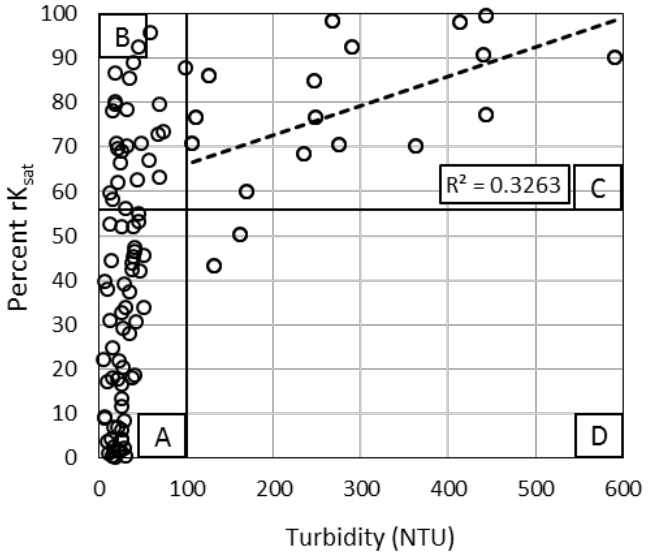

Figure 4.4. Percent reduction in saturated hydraulic conductivity (rK_{sat}) compared to the turbidity observed for soils equilibrated with various irrigation treatment solutions (Figure 4.1). The solid vertical line represents the threshold for stable and unstable aggregates in terms NTU (Zhu et al. 2016), while the solid horizontal line represents the rK_{sat} associated with the flocculation/dispersion threshold for the soil in Quirk and Schofield (1955). Quadrants A through D and the regression are explained in the text.

4.5.2 Changes in threshold with rapidly diluted samples

Based on the C_{TH} at rK_{sat}=10%, we compared the observed rK_{sat} for the soils and plotted these against the calculated C_{TH}, which demonstrated that the calculated results did not always fit observed results, and in the case of Soil 3 failed to fit the observed results at all. Small deviations from the C_{TH} may be argued as fitting within the error of calculation, but to completely fail on all accounts suggests that the approach should not be used. In fact, our results highlight that the C_{TH} is better defined by the approach of rK_{sat} rather than flocculation/dispersion conditions. Quirk (2001) suggests that the C_{TH}, as measured by rK_{sat}, effectively supplies a safety factor for practical implementation of irrigation guidelines. In this work, we applied the same safety factor of 4 (C_{TU}/4) and still the advice based on P_{TEC} would have caused rK_{sat} in the order of 28–47% for Soil 3. This demonstrates the practical value of an rK_{sat} approach where the key factor influenced by the irrigation solution concentration is the soil pore hydraulic network.

It is not possible to determine what rK_{sat} the measured C_{TU} represents as the samples were rapidly diluted and the rK_{sat} values in Table 4.4 no longer relevant to the actual solutions the data points were obtained in. Both the titration and observational approach to measuring C_{TU} appear to be valid in producing somewhat similar results. However, how this applies to a soil hydraulic network remains unknown from this work, and should be further investigated to assign the magnitude of practical relevance to the P_{DIS} approach. Comparing the observed reductions to the positioning of the C_{TU} on the graph against the experimental solutions (Figure 4.3) suggest that C_{TU} is soil-specific, which is something that we would expect given the results of McNeal and Coleman (1966), and Bennett and Raine (2012). This supports the notion that the *flocculation/dispersion* threshold in Figure 4.4 may indeed move well into Quadrant B depending on the soil. Therefore, there would be value in future work determining the rK_{sat} at this threshold and relating it to the C_{TH} in terms of rK_{sat} for a given soil.

4.5.3 Practicality considerations

The results of this work suggest that the use of hydraulic reduction alongside the flocculation/dispersion condition is required to troubleshoot the uncertainty within Quadrant B and to confirm that the rapid dilution process has provided a fair measure of C_{TU}. This actually equates to a greater volume of work than undertaking a single C_{TH} using the methods of Bennett and Raine (2012) and Ezlit et al. (2013).

Furthermore, the time required to experimentally determine the C_{TU} using the P_{DIS} approach does not warrant it replacing a direct measure of rK_{sat}. To equilibrate the soil samples with the irrigation solution, assess water dispersible clay at MQSS equilibration solution, rapidly dilute the solution, and then undertake the observational or titration method was either equivalent or in excess of the C_{TH} direct determination methods. Rengasamy (2002) has demonstrated that this method is suitable for already dispersive soils in 'rainfall' simulated environments, however, our results suggest it is limited to this practically and does not offer a reliable alternative method for C_{TH} determination.

4.6 Conclusion

From this work we determined that the P_{DIS} approach to C_{TH} is not reliable or efficient for C_{TH} determination in non-dispersive soils equilibrated with an irrigation solution. Using it to determine the flocculation and dispersion boundary for initially non-dispersive soil appears to have some merit, but only where the aggregates equilibrated are subject to rapid dilution with deionised water. Importantly, the work identified that for some soils reduction of hydraulic conductivity up to 90% occurred where the measured turbidity was within the range of that considered to indicate a stable soil. Further work is required to investigate this phenomena.

4.7 Acknowledgements

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5 Quantifying the aggregation-dispersion boundary condition in terms of saturated hydraulic conductivity reduction and the threshold electrolyte concentration

Dang, A.[1], Bennett, J. McL.[1], Marchuk, A.[1], Biggs, A.[2], and Raine, S.R.[1]*

[1] *University of Southern Queensland, West St, Toowoomba, QLD 4350, Australia*

[2] *Department of Natural Resources and Mines, Tor St, Toowoomba, QLD 4350, Australia*

[*] *Corresponding authour: John.Bennett@USQ.edu.au*

5.1 Abstract

Marginal quality saline sodic water will be important for agricultural production in water limited environments, and has been demonstrated as suitable for irrigation on a soil-specific basis. Suitability is usually demonstrated as the threshold electrolyte concentration (C_{TH}), defined as a 10–20% reduction in saturated hydraulic conductivity. Others have suggested that the aggregate-dispersion boundary may be used as this threshold, which is also known as the threshold turbidity concentration (C_{TU}). Using a saturated hydraulic conductivity approach, this work sought to quantify the extent of reduction at the C_{TU} and compare this to traditional C_{TH} approaches to define the practicality of the thresholds. The C_{TU} was determined as the point where dispersed clay was detected, and subsequently compared to the C_{TH} with the difference between these compared within the measured domain. The reduction in saturated hydraulic conductivity from a Ca dominant stable condition was determined at each threshold value. It was found that saturated hydraulic conductivity at the C_{TU} reduced by between 44 and 78% for the five Vertisol soils investigated, demonstrating that the C_{TU} varied between soils and was substantially more than the 10–20% reduction in hydraulic conductivity at the C_{TH}. Discussion on application of these thresholds to practical irrigation is provided, and suggests that irrigation water quality application can be optimised on a soil-specific basis. Results reinforce that management guidelines should not be based on the C_{TU}, or at the aggregation-dispersion boundary.

5.2 Introduction

Worldwide, marginal-quality saline-sodic (MQSS) water is becoming an increasingly important component of agricultural water supplies, particularly in water-scarce

countries (Qadir et al. 2007b). Though MQSS water could be a strategic resource, there is risk and concern regarding the potential to degrade soil properties such as permeability through long-term application. Use of such marginal quality waters can have strong effects on the levels of both soluble and exchangeable cations in a soil that lead to soil structural deterioration and salt accumulation (Bennett et al. 2016b; Rengasamy & Marchuk 2011; Sumner 1993). Therefore, practical guidelines to inform where use is strategic, or otherwise, are needed.

While it is generally agreed that soils undergo reduction in saturated hydraulic conductivity (rK_{sat}) prior to dispersion occurring, the extent of this reduction and its relation to the threshold electrolyte concentration (C_{TH}) are still contentious (Quirk 2001; Rengasamy et al. 2016) In their pioneering work, Quirk and Schofield (1955) demonstrated that there is, what appears as, a potential minima associated with the absolute stable state of soils in a Ca system. They went on to define a somewhat arbitrary, but measureable, rK_{sat} of 10% from this potential minima to represent the C_{TH}, which they describe as occurring at an electrolyte concentration (EC) approximately one quarter of that where dispersion was first observed for the same sodium adsorption ratio (SAR). The point where dispersed clay first appeared can be thought of as the aggregate-dispersion boundary condition, which will be defined by a specific electrolyte concentration for a given SAR. Quirk and Schofield (1955) define this specific electrolyte concentration as the threshold turbidity concentration (C_{TU}). Mechanistically, the turbidity concentration is the point at which the clay domain is thermodynamically compromised, whereby Brownian motion dislocates clay particles as a result of repulsive pressures overcoming attractive pressures. From Quirk and Schofield's (1955) data, it can be deduced that the C_{TU} occurs at rK_{sat}≈56% for their specific soil. The extent of continued hydraulic reduction past C_{TH} approaching C_{TU} undoubtedly has important ramifications for practical management of soil as a resource.

The C_{TH}, as defined by rK_{sat}=10–25%, has classically been used to inform irrigation water quality suitability guidelines (ANZECC 2000; Bennett et al. 2016b; Bennett & Warren 2015; de Menezes et al. 2014; DNR 1997) where the 10–25% range demonstrates the arbitrary, but measureable, departure for the potential minima (McNeal & Coleman 1966; Quirk 2001; Quirk & Murray 1991; Raine et al. 2007). In essence, use of the C_{TH} in this manner provides a practical buffer in terms of managing

the likelihood or irreparable soil structural damage due to dispersion occurring, which is a direct assertion of Quirk (2001). If the C_{TH} were to be defined as the aggregate-dispersion boundary (C_{TU}), there would be no buffer for error in management of the system; i.e. if management resulted in slightly more hydraulic reduction than predicted, and dispersion occurred, then the irreparable damage is done. Hence, methods that determine the suitability of irrigation solution for application to land based on the aggregate-dispersion boundary condition (C_{TU}) may actually cause considerable damage to the function of the soil resource, due to substantial rK_{sat} beyond the C_{TH}.

As C_{TH} has been demonstrated as soil specific, it stands to reason that C_{TU} would similarly be soil-specific Therefore, this work seeks to quantify the rK_{sat} associated with C_{TU} and in relation to C_{TH}. In doing so, we will prove the hypothesis that rK_{sat} at the $C_{TU}>>rK_{sat}$ at the C_{TH} and provide clarity for the basis of setting irrigation water quality guidelines in terms of solute thresholds.

5.3 Materials and methods

5.3.1 Soil selection and initial characteristics

Soil pH and electrical conductivity (EC) were determined in 1:5 soil:deionised (DI) water using a Radiometer analytical ION 450 Meter. Exchangeable and soluble cations were determined using a Perkin Elmer NexIon-ICP MS (Inductively Coupled Plasma – Mass Spectrometer). The soluble salts were measured in 1:5 soil:deionised (DI) water. For exchangeable cations, the soluble salts were washed with deionised water and then the samples were extracted with 0.5 M NH_4Cl pH adjusted to 7.2 or 8.2 to match the pH of the soil analysed (Marchuk & Rengasamy 2012). These were done using a 1:5 NH_4Cl solution. The extracted soluble cations were put through a centrifuge for 30 mins, and analysed on the ICP-MS to calculate SAR (See: Rayment and Lyons, 2011 – method 15A2). The tendency of aggregates to disperse was assessed by use of the zeta potential (ζ) measured using a Malvern Zetasizer (See: Marchuk and Rengasamy 2012). Clay content in the dispersion was measured by turbidity (NTU) using a NACH 2100N turbiditimeter and converted to dispersed clay content using the method of Zhu et al. (2016).

Table 5.1. Selected physico-chemical properties of five surface soils (0-10 cm soil depth) collected from cotton farms in southeast Queensland using the method described in text

Factor	*Unit*	*Soil 1 Mungana*	*Soil 2 Yarrandoo*	*Soil 3 Corinda*	*Soil 4 Dunholm*	*Soil 5 Maclands*
Location		-27.022, 151.126	-27.23, 151.32	-27.037, 151.125	-27.077, 151.134	-27.020, 151.167
pH		8.6	7.2	7.8	8.0	7.27
EC	dS/m	0.1	0.21	0.13	0.05	0.19
Soluble Cations$_{1:5}$ ($mmol_c/L$)	Na	0.86	0.77	0.09	0.059	1.87
	Mg	0.63	0.52	0.14	0.08	0.27
	K	0.09	0.1	0.01	0.019	0.10
	Ca	1.03	0.76	0.06	0.204	0.45
TCC	$mmol_c/L$	2.61	2.16	0.31	0.36	2.69
Exchangeable Cations *($cmol_c/kg$)*	Na	0.4	0.39	1.03	0.94	3.73
	Mg	8.67	2.87	14.81	10.66	14.52
	K	2.95	0.66	0.96	0.69	1.12
	Ca	25.52	11.66	24.3	14.09	19.87
SAR		0.98	0.96	0.29	0.157	0.19
CROSS		1.13	1.12	0.37	0.22	0.44
ESP	%	1.07	2.5	2.5	3.55	9.51
EDP	%	6.30	5.53	5.14	6.51	12.47
CEC	meq/100g	37.5	15.6	41.1	26.4	39.24
Soil Texture	Australian classification	Clay	Clay	Clay	Clay	Clay
Clay content	%	75	52	61	60	62
Water-dispersible clay	%	53	35	56	52	35
Zeta potential	mV	-22.8	-23	-27	-29	-16
Organic Carbon	%	1.06	1.01	1.02	0.98	1.31
Dispersion as turbidity (NTU)	Spontaneous	650	200	650	124	118
	Mechanical	2050	850	2050	1566	1566

EC, electrical conductivity (dS/m); TCC, total cation concentration ($mmol_c/L$); SAR, sodium absorption ratio; CROSS, cation ratio of soil structural stability; ESP, exchangeable sodium percentage; EDP, exchangeable dispersive percentage (%); CEC, cation exchange capacity (meq/100g).

Five Vertisol soils (IUSS Working Group 2014), were used in this study and collected from cotton farms in southeast Queensland. Soil samples were collected uniformly from a 0–0.2 m depth, air-dried, and gently ground to pass a 2 mm sieve. The initial chemical characteristics of the soils were relatively similar (Table 5.1), with some variation in the mineralogical suite (Table 5.2). Soil pH ranged between 7 and 8.6.

The soil SAR was <1 $mmol_c/L$ and the soil EDP (Exchangeable Dispersive Potential) (Bennett et al. 2016a) was <7 for Soils 1 through 4, while Soil 5 had EDP=12.5. The clay content was generally between 60–75%, although Soil 2 had a lower clay content of 50%, which subsequently coincided with a lower CEC and substantially lower montmorillonite content. Each of the soils before treatment with MQSS water, had zeta potential within the stable aggregate range (0 to -30 mV) indicating that these soils were initially non-dispersive, which was further supported by results for spontaneous dispersion.

To determine the mineralogical composition of the soils XRD analysis was used and clay fractions were separated by sedimentation (Jackson 2005). No addition of dispersing agents or chemical treatments (such as for organic matter or oxide removal) were made to the clay samples. Dry clay samples were finely ground (<2 μm fraction) prior to analysis. The XRD patterns for randomly oriented air-dried samples were recorded with a PANalytical X'Pert Pro Multi-purpose diffractometer using Fe filtered CoKα radiation, automatic divergence slit, 2° anti-scatter slit and fast X'Celerator Si strip detector. The diffraction patterns were recorded from 3 to 80° 2θ with a 0.5 second counting time per step for an overall counting time of approximately 30 minutes. XRD data were assessed using CSIRO software XPLOT for Windows (Raven 1990). Mineralogical phase identifications were first made by comparing the XRD patterns with the International Centre for Diffraction Data (ICDD) database of standard diffraction patterns, and specific clay mineral identification criteria were based on Brown and Brindley (1980) and Moore and Reynolds (1989). Only reflections for crystalline minerals were considered in these analyses. Information about the dioctahedral/trioctahedral structure of the clay minerals was obtained by examination of the 060 reflections of randomly oriented samples.

All 5 soils had a two-component clay mineral suite of montmorillonite (d≈15.8 Å) and kaolinite (d≈7.15 Å) dioctahedral types (060 patterns not shown) in addition to accessory minerals anatase (d≈3.52 Å), hematite (d≈2.70 Å) and the primary mineral quartz (d≈3.34 Å) (Table 5.2). Soil 2 was the only soil dominated by Quartz, whereby the rest were Montmorillonite dominant.

Table 5.2. Mineralogical composition of clays (%) from XRD analysis

Soil	*Montmorillonite*	*Kaolinite*	*Anatase*	*Hematite*	*Quartz*
Mungana	76	10	4	1	9
Yarrandoo	23	21	4		52
Dunholm	72	7	3	1	17
Corinda	62	6	3		29
Maclands	60	7	4	1	28

5.3.2 Threshold electrolyte concentration methodology

The C_{TH} of the soils was determined using a modification of the method presented in Ezlit et al. (2013). In this work we used polyvinyl chloride (PVC) columns of 15 cm height to accommodate the propensity for the soils to swell, even in a pure Ca system. The soil core was 5 cm thick and prepared to an average bulk density of 1.4 g/cm^3. This average density was obtained by as described by Ezlit et al. (2013) and then all cores for that particular soil were prepared to the average density.

The cores were soaked in a $CaCl_2$ (SAR=0) pre-treatment solution, at the respective treatment EC (0.5, 1.0, 2.0, 4.0 or 8.0 dS/m), from the base with an initial hydraulic head of -4 cm, increasing the head to 0 cm over an hour, and then left to saturate for 12 hours. The cores were subjected to $CaCl_2$ in order to produce a state of potential minima (the most stable possible state) as described by Quirk and Schofield (1955) and consistent with the method of Ezlit et al. (2013). The cores were supported in Bucher funnels and allowed to drain for at least 24 h, which allowing for slaking and structural rearrangement to occur, thereafter remaining saturated at all times. Cores were re-saturated and then the pre – treatment solution was applied at a constant head of 2 cm until steady state in hydraulic conductivity was achieved. Steady state was defined as being reached when less than 3% variation was obtained between 5 consecutive hourly readings. Once steady state was achieved the saturated hydraulic conductivity was calculated using Darcy's law. These data were used as the baseline from which rK_{sat} was determined for the subsequent equilibration with treatment solutions. The solutions used for C_{TH} analysis were synthesised to achieve five constant EC values of 0.5, 1, 2, 4, and 8 dS/m, with nine varying sets of SAR concentration (Table 5.3Table 5.3).The target SAR range at each EC was based on SAR range sufficient to cause dispersion at the given EC as defined by Australian and New Zealand Guidelines (ANZECC 2000), while not definitive, tis provided a

reasonable means to set target SAR ranges by EC. This gave a total of 45 individual treatment solutions for which rK_{sat} was calculated. Once the cores had been allowed to drain to induce slaking they were kept at saturation for the entirety of the experimental analysis. Two replicates for each soil were used to determine C_{TH}, creating a total of 90 cores.

Table 5.3. Required amounts of NaCl and $CaCl_2$ for solution preparation for EC sequence 0.5, 1, 2, 4 and 8 dS/m

Sol.	*Na* *(mmol$_c$/L)*	*Ca* *(mmol$_c$/L)*	SAR (mmol$_c$/L)$^{0.5}$	*EC* *(ds/m)*	*Sol.*	*Na* *(mmol$_c$/L)*	*Ca* *(mmol$_c$/L)*	SAR (mmol$_c$/L)$^{0.5}$	*EC* *(dS/m)*
Pre-Treatment	0	80	0	8.0		75.00	5.00	47.43	8.0
	0	40	0	4.0		37.50	2.50	33.54	4.0
	0	20	0	2.0	**5**	18.75	1.25	23.72	2.0
	0	10	0	1.0		9.37	0.63	16.77	1.0
	0	5	0	0.5		4.69	0.31	11.86	0.5
	30.00	50.00	6.00	8.0		77.00	3.00	62.87	8.0
	15.00	25.00	4.24	4.0		38.50	1.50	44.45	4.0
1	7.50	12.50	3.00	2.0	**6**	19.25	0.75	31.43	2.0
	3.75	6.25	2.12	1.0		9.62	0.38	22.23	1.0
	1.87	3.13	1.50	0.5		4.81	0.19	15.72	0.5
	50.00	30	12.91	8.0		78.10	1.90	80.12	8.0
	25.00	15	9.13	4.0		39.05	0.95	56.66	4.0
2	12.50	7.5	6.45	2.0	**7**	19.52	0.48	40.06	2.0
	6.25	3.75	4.56	1.0		9.76	0.24	28.33	1.0
	3.12	1.875	3.23	0.5		4.88	0.12	20.03	0.5
	63.00	17.00	21.61	8.0		78.80	1.20	101.72	8.0
	31.50	8.50	15.28	4.0		39.40	0.60	71.93	4.0
3	15.75	4.25	10.80	2.0	**8**	19.70	0.30	50.86	2.0
	7.87	2.13	7.64	1.0		9.85	0.15	35.97	1.0
	3.94	1.06	5.40	0.5		4.92	0.08	25.43	0.5
	71.00	9.00	33.47	8.0		80.00	0	∞	8.0
	35.50	4.50	23.67	4.0		40.00	0	∞	4.0
4	17.75	2.25	16.73	2.0	**9**	20.00	0	∞	2.0
	8.87	1.13	11.83	1.0		10.00	0	∞	1.0
	4.44	0.56	8.37	0.5		5.00	0	∞	0.5

The rK_{sat} data were fitted with the disaggregation model (Equation 1) in Ezlit et al. (2013) as a function of EC and SAR. The Disaggregation model relates steady state hydraulic conductivity occurring for a given SAR and EC to the most stable condition of a soil — occurring within a Ca dominant system as a potential minima — to formulate a 3-dimensional hydraulic reduction surface. The model uses observed data from laboratory leaching columns to account for soil specificity. The 20%, 40%, 60% and 80% rK_{sat} contour were extracted and plotted for each soil with the 20% reduction contour used to represent C_{TH}. Table Curve 3D Version 4.0 (SYSTAT Software Inc.

2002) was used to fit the equation and MATLAB R2015a (The MathWorks Inc. 2015) was used to extract the C_{TH} contour.

$$rK_{sat} = 1 - \left[\frac{ge^{m\frac{ESP}{100}(x_0)\left[\left(\frac{ESP}{100}\right)^a + b\right]}}{\left\{1 + ge^{m\frac{ESP}{100}(x_0)\left[\left(\frac{ESP}{100}\right)^a + b\right]}\right\}} \right] \text{ at } x > 0 \qquad \text{Equation 5.1}$$

where x_o is the adjusted swelling factor (adjusted to optimise for montmorillonitic and non-montmorillonitic soils) and a, b, g, m, l, s, and f are empirical parameters allowed to auto optimize by the model; N.B. e is an exponent.

5.3.3 Threshold turbidity concentration

According to Quirk and Schofield (1955) the C_{TU} is where clay particulate is first observed in the leachate, but is later defined as equivalent to the aggregate-dispersion boundary (Quirk 2001). As entrainment of dispersed clay may occur towards the surface prior to discharge with leachate, we sought a method that directly measured the aggregate-dispersion boundary. A modified dispersive potential method was used (Marchuk & Rengasamy 2012).

A further set of soil cores was prepared for each soil, as per those for C_{TH} determination. The cores were equilibrated with treatment solutions (Table 5.3), which was determined as the steady state saturated hydraulic conductivity (hydraulic head of 2 cm). Steady state was defined as being reached when less than 3% variation was obtained between 5 consecutive hourly readings. Once the cores were equilibrated, the top 1 cm of soil core was removed and allowed to air dry prior to being gently ground to pass a 2 mm sieve. These equilibrated soil samples formed the basis for C_{TU} determination.

Ten grams of the equilibrated air-dried soil sample for each soil was placed into a 150 ml jar and 100 ml of DI water was added. After upending the jars three times at a rate of one rotation per minute, they were allowed to settle for 4 hours. Samples where the clay remained in suspension after 4 h had the suspension carefully subsampled by pipette and transferred into a test-tube. These suspensions were then titrated with NaCl-$CaCl_2$ solution (prepared for the respective treatment SAR and EC), sufficient to achieve a 0.1 dS/m increase within the tube, every 12 hours until flocculation occurred and the suspension settle completely. Once this point has been reached, the

solution EC and SAR were directly measured and these data used to determine the C_{TU} for the five soils.

The EC and SAR measured in the previous step, were much less than the initial treatment solutions the soil samples were equilibrated to. This was due to the dilution with DI water. Therefore, another five SAR solutions corresponding to the soil's C_{TU} relationship determined previously were prepared within the measured range of EC. Further soil cores for each soil were prepared as per the C_{TH} determination. The same approach to pre-treatment and treatment was used, but the subsequent treatment solutions were matched to the respective C_{TU} (Table 5.4). Soil cores were once again allowed to drain, as per the C_{TH} procedure, and then re-saturated. Once saturated they remained saturated for the entirety of the hydraulic conductivity measurement process. Saturated hydraulic conductivity was measured using a 2 cm hydraulic head and all solutions were run until steady state was reached. Reduction in saturated hydraulic conductivity was determined as reduction from the pre-treatment solutions for each C_{TU}, where SAR=0 (i.e. prepared as $CaCl_2$ for the specified C_{TU}), in Table 5.4.

5.4 Statistical analyses

The C_{TU} points were fitted using linear regression with SAR as the regression factor. The C_{TU} relationship was linear for all soils within the measured domain; N.B. the measured domain varied for each soil. Beyond this domain the relationship was extrapolated for the purpose of comparison to the C_{TH} measured domain (0.5–8.0 dS/m). The C_{TH} was curve-linear for the 0.5–8.0 dS/m measured domain, but could be explained by a linear relationship over the C_{TU} measured domain. Thus, for the purpose of comparison within the C_{TU} measured domain, both the C_{TU} and the C_{TH} were fitted by linear regression with SAR as the regression factor. This allowed the calculation of the 'safety factor' (F_S) that was described by Quirk (2001) as the regression gradient for the C_{TH} divided by the regression gradient at the C_{TU}. That is:

$$F_s = \frac{a_2}{a_1}, \text{where}$$
$$C_{TU} = a_1 SAR + b_1$$
$$C_{TH} = a_2 SAR + b_2 \qquad \text{Equation 5.2}$$

where the regression gradient is defined as 'a_i' and the y-intercept as 'b_j'. Pearson's product-moment correlation coefficient was calculated for all linear regression

equations. Direct comparison of these linear regressions were subsequently undertaken.

5.5 Results and discussion

5.5.1 Reduction in hydraulic conductivity at the turbidity threshold

The observed rK_{sat} for the five soils tested confirms the hypothesis that rK_{sat} at the C_{TU}>>rK_{sat} at the C_{TH} (Figure 1; Table 5.4). The rK_{sat} at the C_{TU} ranged between 43–55, 42–46, 55–78, 65–75, and 33–52% for Soils 1 through 5, respectively, for the measured SAR range (Table 5.4). In comparison, the C_{TH} is defined as either a 10% (Quirk and Schofield 1955) or 20% (Ezlit et al. 2013) reduction in hydraulic conductivity, meaning that for the 5 soils the C_{TU} produced a further reduction in saturated hydraulic conductivity of 38–51% or 28–41%, on average, as compared to $C_{TH\text{-}Quirk}$ and $C_{TH\text{-}Ezlit}$, respectively.

Notably, the rK_{sat} associated with the C_{TU} increases with increasing SAR and EC, suggesting that grater reduction in hydraulic conductivity can be tolerated prior to dispersion as a result of osmotic potential (increased EC). This equated to 12, 4, 23, 10, and 20% further decrease associated with a 0.40, 0.47, 0.42, 0.66 and 1.18 dS/m increase in EC (increase in EC from the minimum to the maximum EC directly tested) for Soils 1 through 5, respectively. Due to the dilution method used and the initial SAR values on the equilibrated soil samples, the rK_{sat} relationship for C_{TU} was existed within 0.5–1.7 dS/m domain. Within this domain, the C_{TU} was represented by a linear relationship with SAR yielding R^2>0.88 for all soils (Table 5.5). Beyond the measured domain (i.e. C_{TU}>1.5 dS/m) if the linear trend is assumed to be correct (Figure 1), then where the applied irrigation water has an EC=3.0 dS/m — an arbitrary value, but utilised in industry where marginal quality saline sodic water is used for agricultural production (Bennett et al. 2016b; Qadir & Oster 2004) — the associated rK_{sat} for this C_{TU} value is 95, 83, 96, 81, and 77% for Soils 1 through 5, respectively. Such reduction in hydraulic conductivity prior to dispersion occurring is substantial, and it is advised that further testing within this predicted domain would be required. Interestingly, the observed reduction for Soil 4 (75%) was not far removed from the predicted rK_{sat} results of 81%, suggesting that such reduction while substantially could entirely be real. For the five soils there was no general agreement in terms of the reduction magnitude, although it is evident that the observed rK_{sat} associated with the C_{TU} is

much greater than the 20% or 10% rK_{sat} values associated with the C_{TH} by Ezlit et al. (2013) and Quirk and Schofield (1955), respectively.

Table 5.4. Sodium adsorption ratio (SAR) data at the threshold turbidity concentration (C_{TU}) for soils 1 through 5, with the predicted reduction (calculated from the Ezlit et al 2013 model for the observed C_{TU} at the given SAR) and observed reduction in saturated hydraulic conductivity.

Soil	C_{TU} *(dS/m)*	*SAR*	*Pred* rK_{sat} *(%)*	*Obs* rK_{sat} *(%)*	*Soil*	C_{TU} *(dS/m)*	*SAR*	*Pred* rK_{sat} *(%)*	*Obs* rK_{sat} *(%)*
	0.56	6.64	45.7	43.2		0.58	6.48	67.1	65.2
	0.68	8.54	47.3	48.6		0.74	8.55	67.8	70.2
1	0.78	10.08	52.8	52.0	4	0.90	10.62	68.8	68.2
	0.86	11.36	51.9	51.0		1.10	13.16	70.7	70.8
	0.99	13.43	55.0	54.8		1.24	14.99	71.9	75.4
	0.46	5.25	44.9	42.2		0.50	4.14	38.5	32.5
	0.59	6.55	45.6	44.9		1.01	9.24	39.3	33.9
2	0.76	8.19	45.6	44.7	5	1.23	11.44	42.0	40.0
	0.80	8.64	45.3	45.2		1.50	14.15	46.1	47.6
	0.93	9.91	46.0	45.7		1.68	15.90	49.3	52.1
	0.63	7.80	59.9	55.0					
	0.73	9.46	65.3	61.0					
3	0.84	11.17	69.3	75.7					
	0.93	12.55	72.1	70.2					
	1.05	14.44	76.0	77.9					

5.5.2 Relationship between electrolyte and turbidity threshold concentration

Quirk (2001) suggests that the C_{TU} is approximately ¼ that of the C_{TH}, meaning that the C_{TH} provides a 3–4 fold safety factor (Equation 2) in terms of inducing dispersion. Given the extent of hydraulic reduction in our work, we sought to investigate how general this safety factor might be given that the C_{TH} has clearly been established as soil specific (Bennett et al. Submitted; Bennett & Raine 2012; McNeal & Coleman 1966). The relationships between $C_{TU\text{-}}$ and $C_{TH\text{-}Quirk}$ (rK_{sat}=10%) as well as $C_{TH\text{-}Ezlit}$ (rK_{sat}=20%) are shown in Table 5.5, and assumed to be linear for the measured domain; this assumption was fair for the purpose of comparison (R^2>0.98 for all five soils) in the low-EC measured domain, but it is acknowledge here that the actual relationship between C_{TH} and SAR is curve-linear. For Soils 1 through 3 and Soil 5 the safety factor between the C_{TU} and $C_{TH\text{-}Quirk}$ ranged between 1.9 and 10.1. Soil 4 produced a safety factor of 321.5, which was an artefact of very quick initial reduction in hydraulic conductivity associated with increasing SAR at a given EC, subsequently this reduction rate became more gradual. Irrespective of such result, it is clear that that C_{TU} is similarly soil specific in terms of the associated safety factor. This is not

unexpected, and indeed was demonstrated by Marchuk and Rengasamy (2012), but was reported as a soil-specific C_{TH} response occurring at the aggregation-dispersion boundary. However, our work confirms quite clearly that the C_{TU} and the C_{TH}, as defined by the pioneering work of Quirk and Schofield (1955), are distinctly different thresholds and that C_{TU} is general much less than C_{TH}.

While C_{TU} is represented follows a similar linear relationship within the measured domain, there is extreme departure from C_{TH} in the extrapolated domain. The rK_{sat} curves for 20 through 80% follow a curve linear trend with respect to the Ezlit et al. (2013) semi-empirical model; that is, they are determined by a direct reduction in saturated hydraulic conductivity, rather than a specific physicochemical boundary. While the C_{TH} concept is related directly to hydraulic reduction, the C_{TU} concept is related to a specific boundary where aggregates disperse into soil separates. It is possible that the relationship is curve-linear for C_{TU} and simply requires measured data within the predicted domain, but it also raises interesting discussion about whether we should expect C_{TU} to be represented by a consistent rK_{sat}. Bennett et al. (Submitted) observed that the soil-specific volume change in the clay domain at the C_{TH} was apparently not related to the absence or presence of organic matter in the soil (R^2<0.03). On the other hand, Tisdall and Oades (1982) suggest that organic matter has inherently important function in binding aggregates even at the sub-micron level. We believe that it is possible that the C_{TU} occurs at much greater rK_{sat} as C_{TU} increases due to interaction between osmotic pressure and the effect of organic matter physically bonding clay domains. That is, that the organic matter does not become important until the aggregate-dispersion boundary is approached, in terms of its physical effect on binding clay together. This suggests that the disaggregation pressure within the clay domain is greater than the force by which the organic matter binds the particles together, which may explain why greater rK_{sat} is tolerated prior to dispersion at greater C_{TU}. Our data cannot confirm this, but suggests it is a useful hypothesis to test.

Table 5.5. Comparison for the five soils of the threshold turbidity concentration (C_{TU}) with the threshold electrolyte concentration as defined by Quirk and Schofield (1955) ($C_{TH\text{-}Quirk}$; 10% reduction) and Ezlit et al. (2013) ($C_{TH\text{-}Ezlit}$; 20% reduction) in terms of the management 'safety factor' (Equation 2). The relationship for C_{TH} has been assumed as linear for the purpose of comparison to C_{TU} for EC=0-1.5 dS/m; within this EC domain the linear assumption produced an R^2>0.98 in all cases for C_{TH}.

Soil	Statistic	C_{TU}	$C_{TH\text{-}Ezlit}$	$C_{TH\text{-}Quirk}$
1	Relationship	=0.064SAR+0.130	=0.183SAR+0.072	=0.219SAR+0.371
	Saftey Factor		2.8	3.4
2	Relationship	=0.101SAR-0.073	=0.113SAR+0.416	=0.129SAR+0.705
	Saftey Factor		1.1	1.3
3	Relationship	x=0.064SAR+0.128	=0.392SAR-0.247	=0.644SAR+0.021
	Saftey Factor		6.1	10.1
4	Relationship	=0.078SAR+0.075	=9.785SAR-2.59	=25.06SAR-3.14
	Saftey Factor		125.5	321.5
5	Relationship	=0.099SAR+0.088	=0.150SAR+0.299	=0.187SAR+0.660
	Saftey Factor		1.5	1.9

5.5.3 Validation of the disaggregation model for turbidity threshold concentration determination

The observed rK_{sat} in comparison to that directly taken from the 3-Dimensional rK_{sat} surface as produced by the semi-empirical disaggregation model of Ezlit et al. (2013) is presented in Figure 5.2. In terms of the relationship between observed and predicted, the 1:1 line explained greater than 89% of the variation (R^2=89.7), suggesting that predicting the rK_{sat} at the C_{TU}, where SAR is known, is a reasonable approach.

5.5.4 Towards meaningful irrigation water quality guidelines

Use of C_{TU} as the guideline for marginal quality saline-sodic water strategic use is not advisable, given the magnitude of reduction within the observed domain (0–1.5 dS/m). Furthermore, the aggregate-dispersion threshold (C_{TU}) has no safety buffer, which the use of C_{TH} provides to a reasonable degree. The determination of these thresholds is done on the basis of saturated conditions with no direct inclusion of a measure for rapid dilution due to rainfall. Ali et al. (2018) demonstrated that gypsum acting as an electrolyte buffered soil structure from dispersion when the EC was reduced rapidly. This same reasoning is the assertion of Quirk and Schofield (1955) that C_{TH} is the practical threshold as the extra electrolyte allows dilution from rainfall to occur with reduced chance of irreversible hydraulic reduction. Therefore, equating the C_{TU}

aggregation-dispersion boundary with irrigation practical guidelines has a large inherent risk, and should not be advised.

de Menezes et al. (2014) discuss that for some soils an rK_{sat}>20% may indeed be tolerable, especially where that soil had extremely high saturated hydraulic conductivity to begin with (e.g. soils within the sand–sandy associated texture classes), while for other soils any rK_{sat} may be irrelevant in terms of irrigation suitability based on an initially extremely low saturated hydraulic conductivity. The latter situation would suggest irrigation is not feasible irrespective of water quality, while the former situation begs the question of "what rK_{sat} is tolerable?" We contend that to answer this question, the C_{TU} should not be breached, as '*tolerable reduction*' should be practically defined as minimising environmental harm. In this case, if the rK_{sat} is less than observed at the C_{TU} then the change in saturated hydraulic conductivity is theoretically reversible (Quirk & Aylmore 1971; Quirk & Murray 1991; Quirk & Schofield 1955), as clay domain volume expansion due to diffuse double layer development can be compressed provided the domain has not actively dispersed. The size of clay domains will affect the point that Brownian motion dislocates particles and disperses domains, meaning that smaller domains would be expected to disperse prior to larger ones. For this reason, hydraulic conductivity reduction should be reversible to some extent, but not expected to be completely reversible. Hence, the extent of '*reversibility*' may also affect the use of irrigation guidelines beyond the C_{TH} and prior to the C_{TU}.

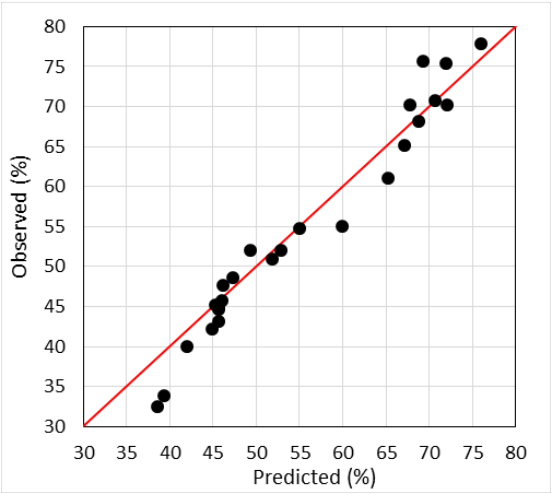

Figure 5.1. Percent reduction in hydraulic conductivity for Soils 1 through 5 at the threshold turbidity concentration as observed by direct measurement, and compared to that predicted by the semi-empirical model of Ezlit et al. (2013). The red line represents the 1:1 line.

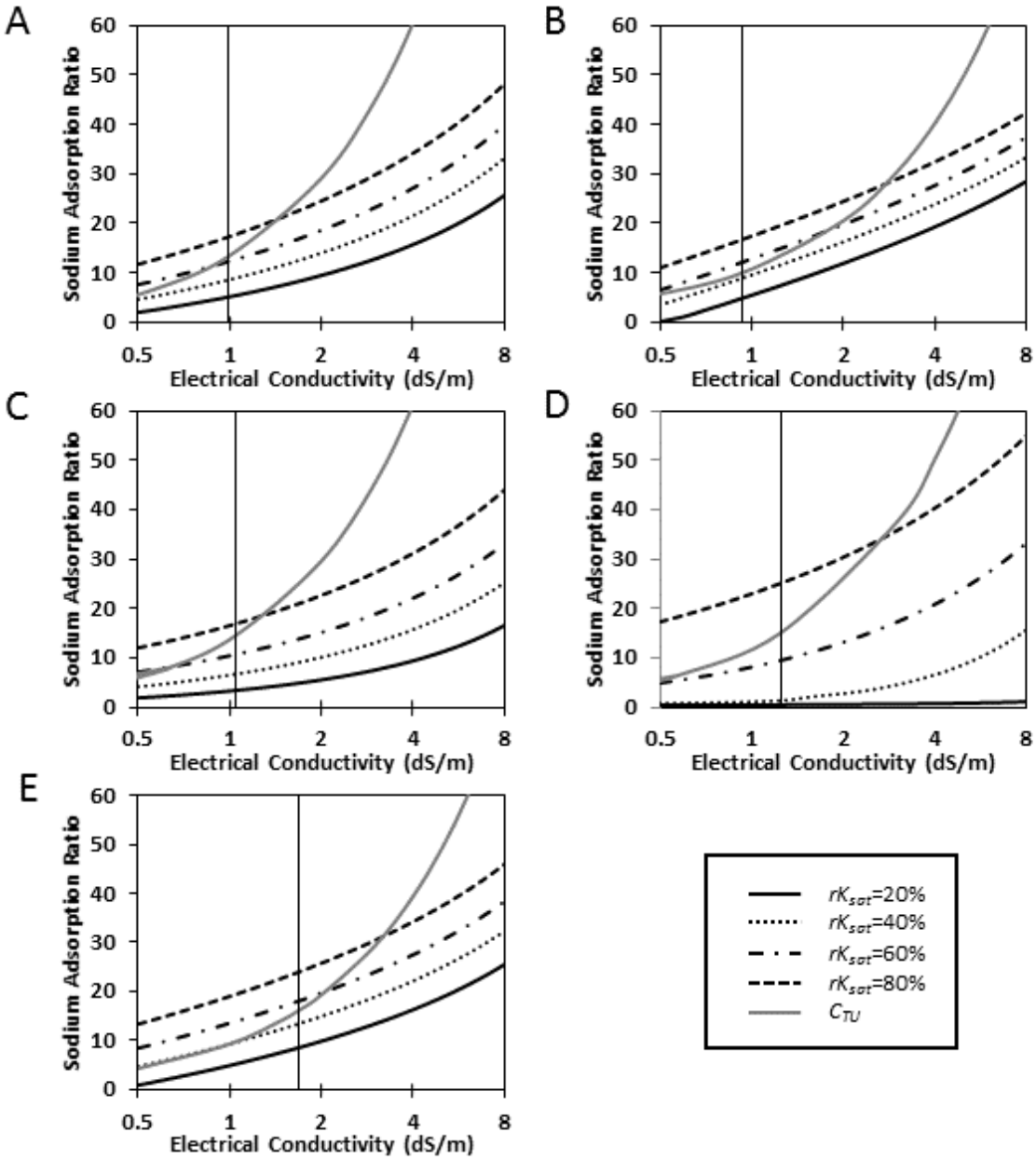

Figure 5.2. Reduction in saturated hydraulic conductivity (rK_{sat}) for: A) Soil 1, B) Soil 2, C) Soil 3, D) Soil 4, and E) Soil 5, where rK_{sat}=20% is the threshold electrolyte concentration (Ezlit et al. 2013) and C_{TU} is the threshold turbidity concentration. The vertical black line within the graph represents upper limit of the C_{TU} measured domain; beyond this point the curve is a forecast, rather than direct measurement. N.B. the x-axis is logarithmic with base 2.

5.6 Conclusion

The C_{TU} was demonstrated as being less than the C_{TH} and the associated rK_{sat} at the turbidity threshold ranging between 44 and 78% for the five Vertisol soils investigated. This confirms that rK_{sat} is much greater at the C_{TU} than at the C_{TH}. This result reinforces that management guidelines should not be based on the C_{TU}, or at the aggregation-dispersion boundary as measured in clay-solute suspensions from water dispersible

clay (this being equivalent to the C_{TU}). This work suggests that irrigation water quality application can be optimised on a soil-specific basis, provided the rK_{sat} deemed tolerable lies between that observed at the C_{TU} and C_{TH}, and careful monitoring ensues.

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6 Towards incorporation of potassium into the disaggregation model for determination of soil-specific threshold electrolyte concentration

Dang, A.[1], Bennett, J. McL.[1], Marchuk, A.[1], Marchuk, S.[1], Biggs, A.[2], and Raine, S.R.[1]*

[1] *University of Southern Queensland, West St, Toowoomba, QLD 4350, Australia*

[2] *Department of Natural Resources and Mines, Tor St, Toowoomba, QLD 4350, Australia*

[*] *Corresponding authour: John.Bennett@USQ.edu.au*

6.1 Abstract

Use of non-traditional irrigation sources will increase with industry water demand, with many industry wastewaters (e.g. agri-industry processes such as milk factories, piggeries, wineries and abattoirs) containing appreciable K, and K known to result in soil structural decline if concentration is sufficient. The C_{TH} is generally understood to represent the electrolyte concentration (directly proportional to electrical conductivity) at which a soil will remain stable when subjected to a given SAR solution, without limiting dispersion (Quirk and Schofield 1955; McNeal and Coleman 1966). However, current approaches to determine C_{TH} do not incorporate K. Hence, this work seeks to investigate incorporation of K into the disaggregation model for C_{TH} and validate this against equivalent Na systems using an ionicity approach. It was found that a single generalised coefficient of equivalence for K relative to Na does not appropriately describe the system changes, rather which this coefficient is specific to a soil and appears to vary with the percolating electrolyte concentration. Incorporation of K into the disaggregation model, while not accurate with a universal coefficient of equivalence for K, was considered reasonable where no other approach could be used. This conclusion was drawn on the basis that the model would serve to produce a conservative C_{TH} under such circumstances, which would not cause undue degradation to the soil environment.

6.2 Introduction

Irrigation is increasingly important at the global scale given an increasing population and demand on food and fibre, as well as a finite land resource. However the growing scarcity of good quality water in arid and semi-arid regions has led to an increased usage of saline-sodic marginal water for irrigation (Shainberg and Gal 1982; Scott *et*

al. 2004; Qadir *et al.* 2007; Ali et al. 2018). Saline-sodic water, though potentially a strategic resource for irrigation, has the prospect to cause soil structural degradation due to elevated concentration of sodium, potassium and/or magnesium (Rengasamy and Marchuk 2011; Smith *et al.* 2015; Bennett *et al.* 2016a). Therefore, adequate management approaches and identification of suitable land for irrigation are paramount to the use of such irrigation waters while avoiding major salinity and sodicity issues (US Salinity Laboratory Staff 1954; Arienzo *et al.* 2009; Jayawardane *et al.* 2011; de Menezes *et al.* 2014; Bennett and Warren 2015; Bennett *et al.* 2016b).

Sodium adsorption ratio (SAR; Equation 6.1) has been the traditional measure to define soil sodicity and the effects of sodium on soil structure, from the point of view of irrigation solution, because sodium is considered to be the dominating salt in dispersive soils, globally. However, naturally occurring soils, as well as irrigation water sources (both natural and recycled), may contain sufficient potassium and/or magnesium to induce dispersion. Studies have shown that K and Mg ions in the exchange complex can cause clay dispersion even when the exchangeable Na levels are minimal (US Salinity Laboratory Staff 1954; Rengasamy 2006; Smiles 2006; Rengasamy and Marchuk 2011; He *et al.* 2013; Bennett *et al.* 2016a). Hence, it is prudent to consider soils from a dispersive, rather than solely sodic, perspective.

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \qquad \text{Equation 6.1}$$

Recent work considers the comparative role of K and Mg in dispersion, relative to Na. Whilst K is similar to Na, being a monovalent cation, the role of K in decreasing permeability through swelling, dispersion and clay migration (Quirk and Schofield 1955), needs to be considered in terms of the hydrated radius and the valence. Arienzo *et al.* (2009) identified that K is often found in high concentrations in wastewaters from agri-industry processes, the long term application of such leading to decreased hydraulic conductivity of the receiving soils (Arienzo *et al.* 2009). The effect of K on soil structure has been debated in the literature and it has been found to have equal or lesser effect than sodium (Chen *et al.* 1983; Robbins 1984; Smiles and Smith 2004). The varying effect of K described by different researchers may be attributed to differences in clay mineraology of the soils studued, and differing sample preparation procedures used by those researchers.

The cation ratio of soil stability (CROSS; Equation 6.2) was developed to replace SAR. It considers K and Mg and attributes a coefficient of equivalence of 0.556 to K relative to Na (Rengasamy and Marchuk 2011). However, this number is actually derived from an arithmetic mean of four concentrations (Rengasamy and Sumner 1998). It is possible that such coefficients are actually soil specific and while the variability observed between coefficients of a particular soil may appear small, the influence of this small difference on dispersion may well be large. Accordingly, Smith *et al.* (2015) discusses that the coefficient of equivalence is variable between soils and can be effectively optimised using statistical and computational approaches, on a soil-specific basis.

$$CROSS = \frac{Na + 0.556K}{\sqrt{\frac{Ca + 0.6Mg}{2}}} \qquad \text{Equation 6.2}$$

We hypothesise that the coefficient of equivalence is soil-specific, and that increasing K in solution results in declining soil hydraulic conductivity. Therefore, it is important that K is considered in soil hydraulic conductivity models. Ezlit *et al.* (2013) improved upon the McNeal and Coleman (1966) clay swelling model modifying it to produce a 3-dimensional hydraulic reduction surface using a semi-empirical approach, based upon solution SAR and the electrical conductivity (EC) of the soil solution. Thus, the 'clay swelling model' effectively describes disaggregation (changes in aggregate stability) for all soils, rather than smectitic ones alone. The disaggregation model (Ezlit *et al.* 2013) relates steady state hydraulic conductivity occurring for a given SAR and EC to formulate a 3-dimensional hydraulic reduction surface. The approach is semi-empirical, as the threshold electrolyte concentration (C_{TH}) is soil-specific (Bennett and Raine 2012), and relies on observed values to predict the full surface and C_{TH} with accuracy. In its current form, the model is only capable of considering Na and Ca systems, which will be inaccurate for soils or irrigation waters with high concentration of K. Hence, this work aims to incorporate K into the disaggregation model. While Mg is known to have an effect on soil structure (Rengasamy and Marchuk 2011; Smith *et al.* 2015), the extent of this effect is more contentious than that of Na with the resulting effect more complex in its prediction (Levy and Feigenbaum 1996; Bennett *et al.* 2016a). Hence, this work focusses on K as the first step.

6.2.1 Theoretical approach

The C_{TH} is a practical defining measure of irrigation water suitability on a soil-specific basis and describes the point where a 20% reduction in hydraulic conductivity occurs (Ezlit et al. 2013). It represents the electrolyte concentration where a soil will remain stable when subjected to a given sodium adsorption ratio (SAR) solution (Quirk and Schofield 1955; McNeal and Coleman 1966; Raine *et al.* 2007; Bennett and Raine 2012; Ezlit *et al.* 2013; de Menezes *et al.* 2014). The C_{TH} is somewhat arbitrary in its discrete existence, as increasing Na concentration causes a gradual decline in hydraulic conductivity. Therefore, C_{TH} is usefully defined as a tolerable percent reduction in hydraulic conductivity resulting from increasing volume of the clay domain (disaggregation) rather than clay dispersion (Dang et al. 2018). To this extent it represents a boundary for safe use of an irrigation water quality (Quirk and Schofield 1955; McNeal and Coleman 1966). Some authors contend that the point of dispersion is the threshold of interest, but the data of Quirk (2001) demonstrates that there is a decline in hydraulic conductivity approaching 56% prior to spontaneous dispersion occurring, and that there is a potential minima associated with absolute stability in a Ca dominant soil. In this work the C_{TH} is defined as a 20% reduction in hydraulic conductivity (rK_{sat}), as per Ezlit *et al.* (2013).

The Disaggregation model (Ezlit *et al.* 2013) relates steady state hydraulic conductivity occurring for a given SAR and EC to formulate the 3-dimensional hydraulic reduction surface as follows:

Flocculation condition:

$$rK_{sat} = 1, at\ x \leq 0 \qquad \text{Equation 6.3}$$

Disaggregation condition:

$$rK_{sat} = 1 - \left[\frac{ge^{m\frac{ESP}{100}(x_0)\left[\left(\frac{ESP}{100}\right)^a + b\right]}}{\left\{1 + ge^{m\frac{ESP}{100}(x_0)\left[\left(\frac{ESP}{100}\right)^a + b\right]}\right\}} \right] \text{ at } x > 0 \qquad \text{Equation 6.4}$$

where rK_{sat} is the reduction in saturated hydraulic conductivity; *ESP* is exchangeable sodium percentage (Equation 2.14); x_o is the adjusted effective swelling factor which takes account of the swelling and dispersion that controls rK_{sat} dynamics; and, *a, b, g, m* are all optimisable empirical fitted parameters dependent on soil type.

In the formulation of Equation 6.2, the ESP is used directly, and x_o is further influenced by the ESP. Hence, in redeveloping the mathematical relationships from SAR to CROSS, K needs to be incorporated into the ESP equation (Equation 2.14). The model utilises ESP on the basis that the observed reduction is a function of the solution parameters SAR and EC, but is also a function of the clay cation exchange capacity (CEC); that is, the disaggregation observed occurs as a result of exchange properties that should be included in the calculation.

Bennett *et al.* (2016a) introduced the exchangeable dispersive percentage (EDP), which takes into account both K and Mg in assessing the dispersive likelihood for a given soil:

$$EDP = \left(\frac{[Na] + a[K] + c[Mg]}{CEC}\right) 100 \qquad \text{Equation 6.5}$$

where all exchangeable cation concentrations, represented by square parentheses, are in $cmol_c/kg$ and the coefficients of equivalence a and c are optimisable (See: Smith *et al.* 2015; Bennett *et al.* 2016a). However, where coefficients are not able to be optimised, average solutions are used where a=0.556 and c=0.037. The c [Mg] term is not used in this research unless it is considered to be 40% effective (i.e. 40% effective as compared to a pure Mg system). This was due to Mg having both a positive and negative effect on the prediction of dispersive extent equivalent to Na, nominally related to the concentration of Mg existing in comparison to all other cations (see Bennett et al 2016). Given this, the current work will not consider Mg experimentally, but does provide a lead in to how it might be included in formulation from a dispersive frame of reference.

In considering that the coefficients transfer the concentration of K and Mg into an equivalent Na concentration, we can calculate the total effective Na concentration (total sodium) for the system (Na_T):

$$Na_T = Na + Na_K + Na_{Mg}, \text{ where } Na_K = aK, \quad Na_{Mg} = cMg \qquad \text{Equation 6.6}$$

As for EDP, the concentrations are in $cmol_c/kg$. Accounting for the cations other than Na in terms of their equivalent dispersive extent provides a mathematical solution to incorporating the differential dispersive effects as a single factor relatively simply through an effective ESP:

$$effective\ ESP = EDP = \left(\frac{Na_T}{CEC}\right)100 \qquad \text{Equation 6.7}$$

By substitution of Equation 6.7 into Equation 6.4 we find:

$$rK_{sat} = 1 - \left[\frac{ge^{m\frac{EDP}{100}(x_0)\left[\left(\frac{EDP}{100}\right)^a+b\right]}}{\left\{1+ge^{m\frac{EDP}{100}(x_0)\left[\left(\frac{EDP}{100}\right)^a+b\right]}\right\}}\right] \text{ at } x > 0 \qquad \text{Equation 6.8}$$

However, as previously discussed, x_o is also a function of ESP:

$$x_0 = (f)\left((3.6 \times 10^{-4})ESP^*\right)(d^*), \text{ where } ESP^* = ESP - ESP_T \qquad \text{Equation 6.9}$$

The *f* term is an empirical and optimisable coefficient (dimensionless); the ESP^* refers to the adjusted ESP for solution effect and threshold conditions; and, the d^* refers to the corrected adjusted-interlayer-spacing of clay platelets (see Ezlit et al. 2013, p9). McNeal (1968) studied a family of soils from which the ESP_T function (Equation 6.10) was derived. Its value is dependent on the concentration of the solute and is a representation of the point at which K_{sat} begins to decline – the threshold ESP level. The ESP_T value is predicted from soil stability indicators suggested by Quirk and Schofield (1955), specific to each soil due to the variance of solution concentration (C_0) effects on the clay mineralogy, which is why the generic equation replaces the constants with optimisable (on the basis of empirical data) coefficients *l* and *s*:

$$ESP_T = l + s \ln C_0 \qquad \text{Equation 6.10}$$

where *l* and *s* represent parameters that are dependent on the soil type and condition and C_0 is the initial solute concentration.

On the basis of Equation 6.6, we assume that for a system containing cations other than Na alone:

$$ESP_T = EDP_T \qquad \text{Equation 6.11}$$

Thus, substituting Equation 6.7, Equation 6.9, Equation 6.10 and Equation 6.11 provides:

$$EDP^* = EDP - EDP_T \qquad \text{Equation 6.12}$$

$$Therefore\ x_0 = (f)((3.6 \times 10^{-4})EDP^*)(d^*)$$

By means of Equation 6.8 and Equation 6.12 it is therefore possible to mathematically include dispersive effects of K and Mg into the Disaggregation model; noting that dispersive effects of Mg are in reference to Na, and that the flocculative effect of Mg would still differ in respect to Ca, making incorporation of Mg total effect into the Disaggregation model incomplete at this point.

6.3 Methodology

6.3.1 Experimental design

In evaluating the efficacy of Equation 6.8 &Equation 6.12 based on the coefficient of equivalence in Rengasamy and Marchuk (2011), this work tests the hypothesis that:

$$1.8 \times [Na]\ \text{concentration} = [K]\ \text{equivalent concentration}$$

where the [K] equivalent concentration refers to the required K concentration to produce the equivalent Na effect; 1.8 is the inverse of the '0.556' (1/1.8) coefficient for K in Equation 6.2 on the basis that if it is approximately 56% as effective as Na at dispersion then nearly twice as much K would be required to provide the Na equivalent dispersive effect. This is tested by undertaking standard C_{TH} analysis utilising the approach of Ezlit *et al.* (2013) and Bennett and Raine (2012), and then subjecting a sample of the same soil to the equivalent analysis where the K solution is matched to the same effective SAR. If the hypothesis is correct, then the rK_{sat} results should be equivalent. The K was equivalent to the Na while the Ca was adjusted to create and equivalent effect to the Na solution.

6.3.2 Soil selection and preparation

Four distinctly different soils (Table 6.1) were utilised in the work in order to investigate the hypothesis and test the applicability of a generalised coefficient of equivalence for K. Selected descriptive properties for the five soils are displayed in Table 6.1. All soils were ground to pass a 2.0 mm sieve prior to analysis and soil core preparation.

Soil pH and EC were measured using 1:5 soil: water suspensions (equivalent to methods 4A1 and 3A1 from Rayment and Lyons (2011)), while exchangeable cations were measured using 1:5 soil:reagent extractions with 0.5M NH_4Cl, (equivalent to Rayment and Lyons (2011) method 15A2. The exchangeable and permeate soluble

cations were measured using a PerkinElmer inductively coupled plasma – mass spectrometer. These data were subsequently used to calculate the SAR (Equation 6.1), EDP (Equation 6.5) and CROSS (Equation 6.2).

Table 6.1. Selected soil properties of the four experimental soils; classifications as per the Australian Soil Classification (Isbell 2002)

Soil		A	B	C	D
Soil Classification		Brown Chromosol	Brown Dermosol	Brown Vertosol	Black Calcarosol
pH.		8.74	9.1	9.2	8.5
EC	dS/M	0.12	0.15	0.37	0.18
Clay	%	36	42	49	54
Sand	%	60	42	41	38
Silt	%	4	16	10	8
exch.Na	$cmol_c/kg$	0.3	1.6	11.4	1.5
exch.K	$cmol_c/kg$	4.7	0.6	0.9	0.8
exch.Ca	$cmol_c/kg$	77.4	65.5	33.4	61.8
exch.Mg	$cmol_c/kg$	17.6	32.3	54.3	35.9
CEC		12	19.7	29.3	47.1
EDP	%	29.70	15.88	47.47	6.95
SAR		0.11	0.92	5.34	0.99

For each soil, five soil cores were prepared to a height of fifty mm, in PVC tubing (75 mm length, 87.5 mm internal diameter) with No. 1 filter paper placed at the base of the soil core and the core retained at the base by a 1.0x1.0 mm mesh. A generic bulk density for each soil subject to an equivalent settling force was determined. Each soil had three replicates prepared with 400 g of soil in each core. The core assembly was dropped from 50 mm height three times with the resultant bulk density recorded and the results averaged within each soil. Cores were then repacked to 50 mm thickness to the average bulk density.

6.3.1 Soil hydraulic conductivity dynamics

For each soil, the threshold electrolyte concentration was measured for both Na and K using the method of Ezlit *et al.* (2013) and Bennett and Raine (2012). Soil cores were initially wet from the bottom using capillary action under a -40 mm hydraulic head with the head increased to 0 mm (saturation) at a rate of 10 mm hydraulic head/h with $CaCl_2$ (EC 2) solution. At saturation, the pre-treatment was allowed to equilibrate for 12 hours.

This involved the use of a pre-treatment solution of $CaCl_2$ (CROSS 0 – EC 0.5, 1, 2, 4, 8) at the respective EC of each core in order to obtain the benchmark saturated hydraulic conductivity from which to gauge rK_{sat}. The pre-treatment solution is usually created at concentrations equivalent to the total cation concentrations of the first treatments. However in the K C_{TH} analysis, the pre-treatment solutions had to be applied three times at different concentrations to ensure that the treatments with the lower concentrations coincide with a matching pre-treatment (Table 6.2).

Table 6.2. Concentration of the pre-treatment solutions used to equilibrate the cores to the respective EC values

	EC dS/m	K ($mmol_c/L$)	Ca ($mmol_c/L$)	TCC ($mmol_c/L$)
Pre Treat 3	8	0	80	80
	4	0	40	40
	2	0	20	20
	1	0	10	10
	0.5	0	5	5
Pre Treat 2	8	0	59.27	59.27
	4	0	29.64	29.64
	2	0	14.82	14.82
	1	0	7.41	7.41
	0.5	0	3.70	3.70
Pre Treat 1	8	0	45.46	45.46
	4	0	22.73	22.73
	2	0	11.36	11.36
	1	0	5.68	5.68
	0.5	0	2.84	2.84

The soil cores were then subject to both Na K_{sat} analysis and K K_{sat} analysis using a constant hydraulic head of 5 mm using the pre-treatment solution (Table 6.2) until constant flux was achieved (steady state). Once benchmark conditions had been established, treatment solutions (Table 6.3) were applied to the respective replicates with each solution run until steady state conditions had been reached for the treatment solution.

From this point, progressive solutions of increasing SAR and CROSS at the given constant EC were applied to respective cores and run to steady state conditions for each solution combination. The subsequent reduction in saturated hydraulic conductivity (rK_{sat}) was determined from the benchmark condition. This allowed formulation of a 3-dimensional surface from which the threshold electrolyte concentration was calculated as a 20% hydraulic reduction for any given SAR and CROSS.

Table 6.3. Solution cation suite and concentration for the sodium and potassium equivalent systems. The table shows the concentration of the sodium based solutions and the Potassium based solutions; CROSS, cation ratio of soil stability; TCC, total cation concentration

SAR	Na ($mmol_c/L$)	Ca ($mmol_c/L$)	Final TCC ($mmol_c/L$)	CROSS	K ($mmol_c/L$)	Ca ($mmol_c/L$)	Final TCC ($mmol_c/L$)
0	0	80	80	0	0	80	80
0	0	40	40	0	0	40	40
0	0	20	20	0	0	20	20
0	0	10	10	0	0	10	10
0	0	5	5	0	0	5	5
6.00	30.00	50.00	80	6.00	30.00	15.46	45.46
4.24	15.00	25.00	40	4.24	15.00	7.73	22.73
3.00	7.50	12.50	20	3.00	7.50	3.86	11.36
2.12	3.75	6.25	10	2.12	3.75	1.93	5.68
1.50	1.87	3.13	5	1.50	1.87	0.97	2.84
12.91	50.00	30	80	12.91	50.00	9.27	59.27
9.13	25.00	15	40	9.13	25.00	4.64	29.64
6.45	12.50	7.5	20	6.45	12.50	2.32	14.82
4.56	6.25	3.75	10	4.56	6.25	1.16	7.41
3.23	3.12	1.875	5	3.23	3.12	0.58	3.70
21.61	63.00	17.00	80	21.61	63.00	5.26	68.25
15.28	31.50	8.50	40	15.28	31.50	2.63	34.13
10.80	15.75	4.25	20	10.80	15.75	1.31	17.06
7.64	7.87	2.13	10	7.64	7.87	0.66	8.53
5.40	3.94	1.06	5	5.40	3.94	0.33	4.27
33.47	71.00	9.00	80	33.47	71.00	2.78	73.78
23.67	35.50	4.50	40	23.67	35.50	1.39	36.89
16.73	17.75	2.25	20	16.73	17.75	0.70	18.45
11.83	8.87	1.13	10	11.83	8.87	0.35	9.22
8.37	4.44	0.56	5	8.37	4.44	0.17	4.61
33.54	37.50	2.50	40	33.54	37.50	0.77	38.27
23.72	18.75	1.25	20	23.72	18.75	0.39	19.14
16.77	9.37	0.63	10	16.77	9.37	0.19	9.57
11.86	4.69	0.31	5	11.86	4.69	0.10	4.78
62.87	77.00	3.00	80	62.87	77.00	0.93	77.93
44.45	38.50	1.50	40	44.45	38.50	0.46	38.96
31.43	19.25	0.75	20	31.43	19.25	0.23	19.48
22.23	9.62	0.38	10	22.23	9.62	0.12	9.74
15.72	4.81	0.19	5	15.72	4.81	0.06	4.87
80.12	78.10	1.90	80	80.12	78.10	0.59	78.69
56.66	39.05	0.95	40	56.66	39.05	0.29	39.34
40.06	19.52	0.48	20	40.06	19.52	0.15	19.67
28.33	9.76	0.24	10	28.33	9.76	0.07	9.84
20.03	4.88	0.12	5	20.03	4.88	0.04	4.92
101.72	78.80	1.20	80	101.72	78.80	0.37	79.17
71.93	39.40	0.60	40	71.93	39.40	0.19	39.59
50.86	19.70	0.30	20	50.86	19.70	0.09	19.79
35.97	9.85	0.15	10	35.97	9.85	0.05	9.90
25.43	4.92	0.08	5	25.43	4.92	0.02	4.95
Infinity	80.00	0	80	Infinity	80	0	80
Infinity	40.00	0	40	Infinity	40	0	40
Infinity	20.00	0	20	Infinity	20	0	20
Infinity	10.00	0	10	Infinity	10	0	10
Infinity	5.00	0	5	Infinity	5	0	5

6.3.1 Statistical analyses

The differences between rK_{sat} for treatments were investigated using t-tests for sample populations in PASW Statistics 18 (IBM 2009), where the sample populations were

defined as response due to Na and response due to K. Three-dimensional surfaces were created in TableCurve3D (SYSTAT Software Inc. 2002) with the fit and fitted standard deviation analysed.

6.4 Results

Figure 6.1 shows the 3-dimensional rK_{sat} surfaces as a function of soil ESP, or effective ESP (EDP; Equation 6.5), and total solution concentration. In all cases, treating each surface as an individual population (Figure 6.2, Figure 6.3), the range of reduction observed for the Na treatment (ESP) was significantly greater than that observed for the K treatment (effective ESP), indicating that ESP≠effective ESP for the full range of rK_{sat}. In support of this, the model parameters for the corresponding surfaces are vastly different for the same soil indicating the treatments had very different results. Initial rK_{sat} and reduction at low ESP, or effective ESP, resulted in somewhat similar responses between treatments for the same soil, Except for Soil B, depending on the total solution concentration. Subsequently, the C_{TH} curves in Figure 6.2. Threshold electrolyte concentration curves for Soils A—D as determined for traditional sodium adsorption ratio (SAR) and assuming a 0.556 coefficient of equivalence for K with respect to Na (Equivalent SAR). depict the differences observed for the same soils subjected to either a traditional SAR or an equivalent K-SAR. Soil A produces a similar C_{TH} for both Na and K treatments. Soils C and D produce similar threshold results for Na and K treatments at EC<1.0 dS/m, but rapidly become more tolerant than Na thresholds to a given SAR at EC≥1.0 dS/m. However, the results for Soil B are distinctly different between Na and K treatments, whereby the use of an equivalent K-SAR results in a soil with capability to tolerate a much greater SAR at equivalent EC as compared to the Na treatment.

Table 6.4. Model parameters for the fitted surface in Figure 6.1 as predicted from Equation 6.3 and Equation 6.4

Model parameters	*Brown Chromosol*		*Brown Dermosol*		*Brown Vertosol*		*Black Calcarosol*	
	(Na)	*(K)*	*(Na)*	*(K)*	*(Na)*	*(K)*	*(Na)*	*(K)*
a	$1.518\text{x}10^{-5}$	0.0001	0.159	$8.272\text{x}10^{-6}$	0.328	0.697	$1.257\text{x}10^{-5}$	0.259
b	0.326	0.138	$3.970\text{x}10^{-5}$	0.0005	$3.104\text{x}10^{-5}$	4.057	0.279	0.192
g	3.148	0.409	8.304	0.395	3.989	0.264	0.914	0.065
m	2.945	8.996	2.378	4.349	2.720	2.210	8.865	8.746
s	2.669	-1.081	0.736	-1.207	12.121	-0.668	9.527	-0.787
l	-2.494	3.451	-0.660	6.611	-5.096	11.228	-18.548	10.954
f	0.483	-4.047	0.197	-7.125	0.164	-2.538	0.120	-10.49
r^2	0.923	0.955	0.993	0.836	0.929	0.904	0.938	0.768
FitStdErr	0.092	0.057	0.031	0.0999	0.180	0.053	0.139	0.0747

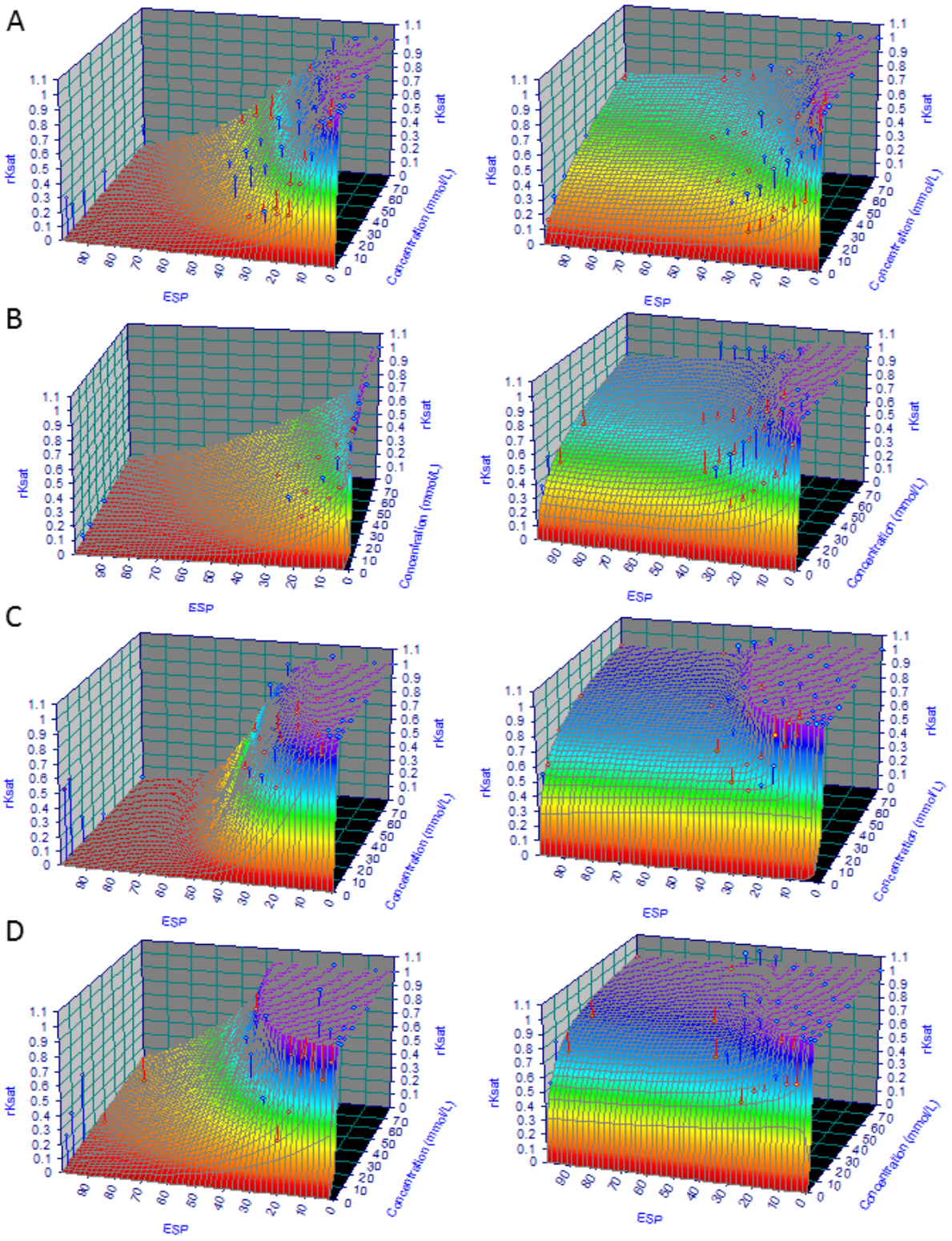

Figure 6.1. Reduction in saturated hydraulic conductivity (*rKsat*) as an inverse ratio — where *kKsat*=1.0=0% reduction and *rKsat*=0.1=90% reduction — for Soil A (Brown Chromosol), Soil B (Brown Dermosol), Soil C (Brown Vertosol) and Soil D (Black Calcarosol). The 3-dimensional surfaces to the left are a function of the exchangeable sodium percentage (ESP) and solution concentration ($mmol_c/L$), while those surfaces to the right are produced from the application of potassium at an effective ESP (EDP; Equation 6.5); model parameters are shown in Table 6.4. The dots of the plots represent the residual measured values.

Where data with rK_{sat}>0.8 was excluded from sample populations, statistical comparison of the remaining data indicated that the K treatment resulted in significantly lower saturated hydraulic reduction (p<0.05) than was observed for the Na treated soils even though the K and Na solutions had been prepared on the basis of equivalence in potential hydraulic effect. Furthermore, direct comparison of the Na-Ca to K-Ca systems observed rK_{sat} demonstrated that there was a clear EC effect on the equivalent effect. As the solution concentration increased, the observed rK_{sat} was less for the K treatment than for the Na treatment, with this result consistent for all four soils (Figure 6.3). These data indicate clearly that there is a poor relationship between the K-Ca and Na-Ca system.

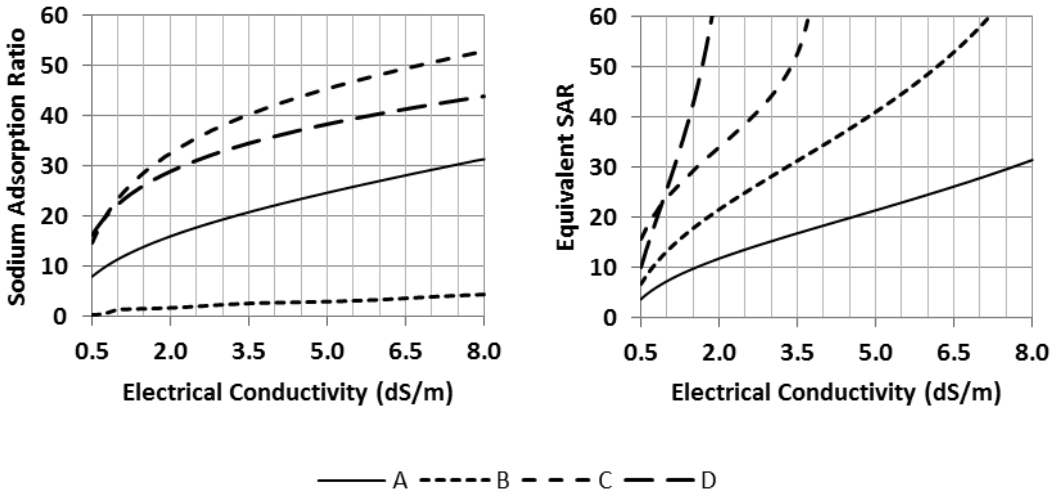

Figure 6.2. Threshold electrolyte concentration curves for Soils A—D as determined for traditional sodium adsorption ratio (SAR) and assuming a 0.556 coefficient of equivalence for K with respect to Na (Equivalent SAR).

6.5 Discussion

6.5.1 Potassium and sodium relative impact

There is clear evidence that K results in reduction of saturated hydraulic conductivity as K concentration increases relative to Ca at a respective EC. However, we cannot accept the experimental hypothesis that:

$$1.8 \times [Na] \text{ concentration} = [K] \text{ equivalent concentration}$$

The coefficient of equivalence (0.556) suggested by Rengasamy and Marchuk (2011) results in a variable effect in terms of hydraulic reduction, compared to an equivalent Na system, and is therefore not a universal coefficient, supporting the notions of Smith

et al. (2015) and Bennett *et al.* (2016a) . This suggests that direct incorporation of K into the disaggregation model through the use of EDP is not as simple as first thought.

A distinct result was observed when comparing the K-Ca to Na-Ca systems in terms of hydraulic conductivity reduction (Figure 6.3), whereby deviation from the 1:1 line was greater for all soils as the soil solution concentration was increased. Furthermore, for all soils a significantly greater hydraulic conductivity was maintained in a homoionic K system than for a homoionc Na system, irrespective of EC, although the difference was greatest as EC increased. This suggests that increasing the solution concentration in a K system has a greater effect on compressing the diffuse double layer than in a Na system (Smith *et al.* 2015). The hydrated radius of K and Na potentially explains these differences, as the hydrated radius for K<Na (Na=3.56 Å, K=3.2 Å), which would physically facilitate a thinner diffuse double layer at the same solution concentration (Conway 1981).

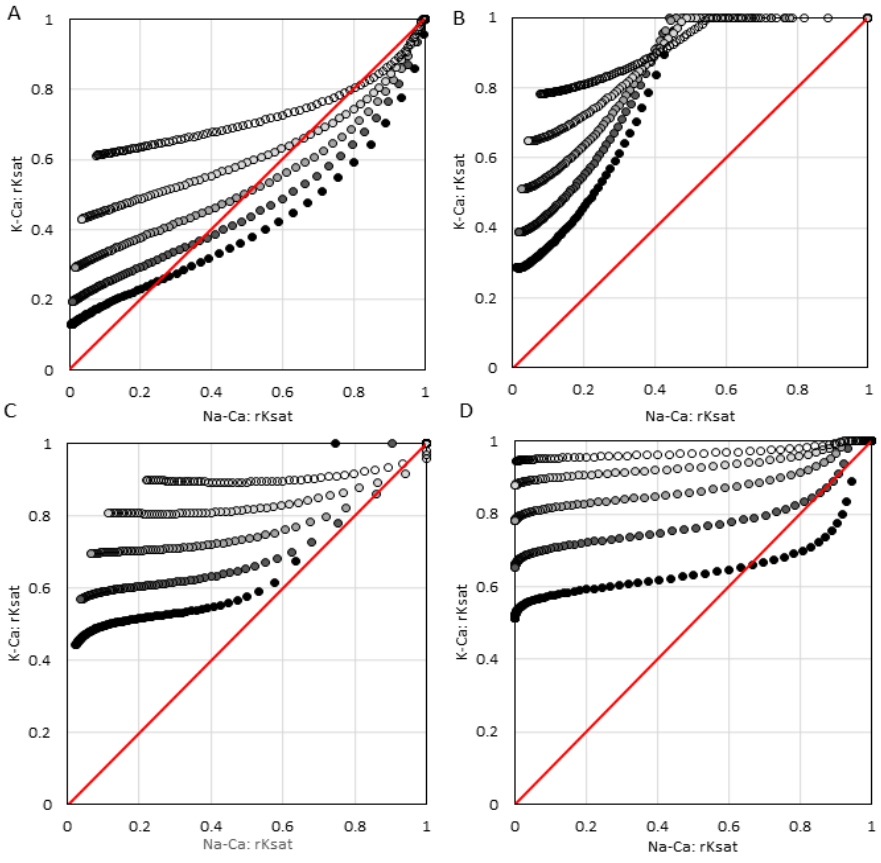

Figure 6.3. Comparison of semi-empirical reduction in saturated hydraulic conductivity (rK_{sat}) results for a K-Ca and Na-Ca system for Soil A (Brown Chromosol), Soil B (Brown Dermosol), Soil C (Brown Vertosol), and Soil D (Black Calcarosol); the red line represents a 1:1 response; Solution EC progresses from white circles (8.0 dS/m) towards black circles (0.5 dS/m) in the order 8.0, 4.0, 2.0, 1.0, and 0.5 dS/m for all soils.

A further likely interacting factor is the potential for illitisation (Marchuk *et al.* 2016). Soils often contain minerals of smectitic origin, directly or as an interstratified form (Norrish and Pickering 1983; Velde 2001; Churchman and Lowe 2012). Marchuk *et al.* (2016) demonstrated that addition of ≈6 pore volumes of wastewater containing 6.39 $mmol_c/L$ of K resulted in a greater presence of illite mineral assemblages, either as an illite-rich inter-layered mineral or illite. In our work, the presence of K increases with the concentration of the solution for the same effective K-SAR, which would provide greater K for illitisation. Additionally, during the rK_{sat} measurement process each soil core passes at least 7 pore volumes per data point in Figure 6.1, approaching at least 70 pore volumes by the end of experimentation. As the ratio of K to Ca in the solution increases as the K-SAR increases, this could well explain the resilience of soils to further hydraulic decline. Where smectitic minerals are subject to illitsation then their potential to change volume within the quasi-crystal is reduced, affecting the total potential for clay domain volume change (Quirk 2001). Therefore, it is entirely possible that the EC effect observed is one where minerals become less expansive due to illitisation, resulting in lower potential for disaggregation (Bennett *et al.* Submitted), as well as greater compression of the diffuse double layer due K occupying less physical space than Na. However, this requires further investigation.

6.5.1 Implications for cation ratio of structural stability

This work supports the view that the coefficient of equivalence for K relative to Na is soil specific. Smith *et al.* (2015) suggested that the coefficients of K and Mg in reference to CROSS (comparable to the K-SAR used in this work) are likely to vary from soil to soil and can be optimised on this basis. They modified the coefficient of equivalence associated with K, with respect to a ratio calculated based on C_{TH}, rather than the flocculation point, centred on the work of Quirk and Schofield (1955). However, the relationship for C_{TH} in Quirk and Schofield (1955) is linear, which has been demonstrated as not the case for the soil aggregate system (McNeal and Coleman 1966; Ezlit *et al.* 2013). Figure 6.4 depicts the coefficient of equivalence for K relative to Na calculated on the basis of C_{TH} as a ratio between the Na and K systems. We observe here that the effectiveness of K relative to Na decreases as EC increases for Soil A, Soil B and Soil D. Soil C slightly decreases, but could be thought of as near constant, which would be an exception to the observation possibly due to clay mineralogy or the cation concentration. Furthermore, it is apparent that K had a greater

initial effect on rK_{sat} than Na for Soil A where the coefficient of equivalence was greater than 1. The data in this work is not sufficient to detail the exact reasoning why, but it is noted that that this sensitivity to K is short lived as K concentration increases; i.e. the Na system still cause a much greater hydraulic reduction than the K system (Figure 6.1, Soil A). These observations do not suggest that the optimisation approach of Smith et al. (2015) is invalid, rather that both the optimised CROSS and the EC must be considered as interacting dependent factors. Hence, as the ratio between the Na and K differences in C_{TH} varies with EC, we suggest that future approaches to improve predictive capabilities of K effects need to consider optimisation against both the CROSS of the solution and the EC of that solution.

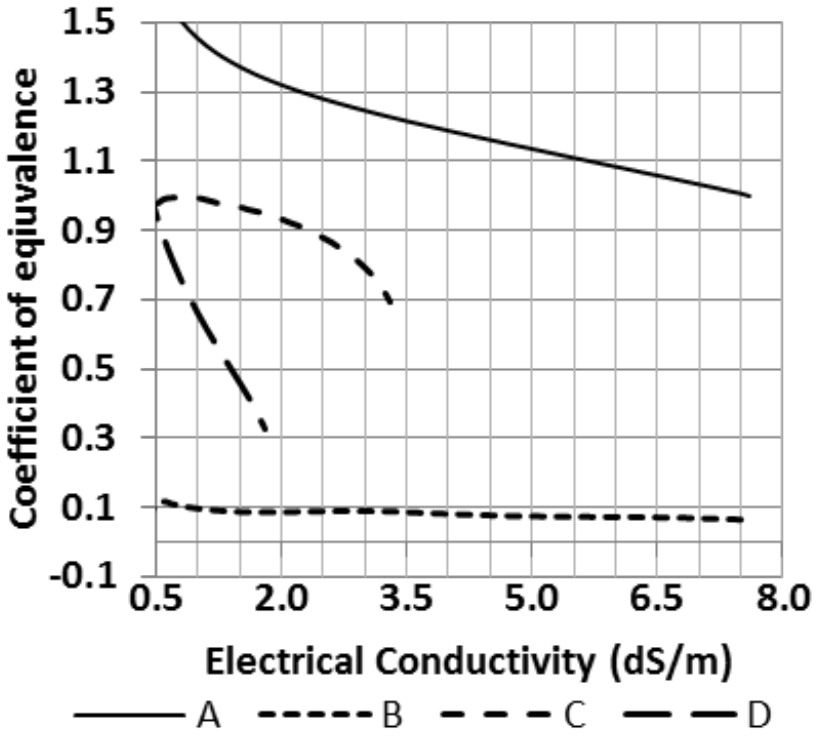

Figure 6.4. Calculated coefficient of equivalence for K relative to Na on the basis of the threshold electrolyte concentration obtained for the K and Na systems for Soil A (Brown Chromosol), Soil B (Brown Dermosol), Soil C (Brown Vertosol), and Soil D (Black Calcarosol).

6.5.1 Incorporation of potassium into the disaggregation model

This work sought to include K into the disaggregation model presented by Ezlit et al. (2013) using the EDP as defined by Bennett *et al.* (2016a). The experimental results suggest that there is a variable effect for K dependent on EC, potentially affected by illitisation. However, we believe it is still possible to incorporate K into the equation in a meaningful way. The approach of using a generic coefficient of equivalence for K

is reasonable as an interim approach, provided the system is not entirely dominated by K, and there is not capacity to determine the specific coefficient. For salinity advised as appropriate under irrigation practice (≈2.0 dS/m), the effect of K was shown to produce rK_{sat} of 20% that could be compared to effects of Na for three of the four soils. Moreover, where the K content was increased, the resulting rK_{sat} was much more conservative for the K system as compared to the Na system. Hence, even in high K concentration systems, the use of the approach presented in this work will simply supply a more conservative recommendation of the C_{TH} where K effect is determined as an equivalent Na concentration in the laboratory-method for C_{TH} presented in Bennett and Raine (2012).

This work suggest that use of Equation 6.4 in the disaggregation model would provide more accurate results where the coefficient of equivalence for K relative to Na is directly measured. To obtain this coefficient there is significant effort that may not be conducive to economic laboratory costs. Therefore, further work should be undertaken in line with Smith et al. (2015), but over a greater range of EC on the same soil, to identify an optimisation equation that could be incorporated into the disaggregation model as a parameter. The effect of illitisation on this optimisation must be afforded greater attention in order to mechanistically represent the system and provide accurate predictions in hydraulic models into the future.

6.6 Conclusion

This work proves that a single generalised coefficient of equivalence for K relative to Na does not appropriately describe the system changes. Instead, it was demonstrated that the coefficient is specific to a soil, supporting optimisation approaches to determine the coefficient. It was observed that effect of K relative to Na varied to a greater extent where the EC of the solution increased, which suggested a greater influence of osmotic potential on compressing the diffuse double layer in K systems, as well as the possibility of illitisation occurring. The suggested approach of using EDP as an effective ESP for incorporation of K into the disaggregation model, while not accurate with a universal coefficient of equivalence for K, was considered reasonable where no other approach could be used. This conclusion was drawn on the basis that the model would serve to produce a conservative C_{TH} under such circumstances, which would not cause undue degradation to the soil environment.

6.7 Acknowledgements

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7 Reduction in saturated hydraulic conductivity as related to the net negative charge of clay

7.1 Introduction

The threshold electrolyte concentration (C_{TH}) provides a measure of the state of soil stability as a function of the percolating solution in terms of sodium adsorption ratio (SAR) and the electrolyte concentration (directly equivalent to electrical conductivity; EC). Classically, this has been defined as a 10–25% reduction in hydraulic conductivity, where reduction is from a state of potential minima in the clay domain (Ezlit et al. 2013; McNeal & Coleman 1966; Quirk 2001; Quirk & Schofield 1955; Raine et al. 2007). The specific reduction percentage is somewhat arbitrary in that it is a measureable departure from the potential minima and constrained by the error of the measurement method. The SAR at the C_{TH} has been demonstrated as soil-specific (Bennett & Raine 2012; Marchuk & Rengasamy 2012; Shainberg & Letey 1984), with specificity conceptually explained as a function of clay content and type (Frenkel et al. 1978), the presence of carbonates and oxides (Deshpande et al. 1964; Oster et al. 1996), and organic matter content (Nelson & Oades 1998). However, the occurrence of the C_{TH} for a particular soil is not currently predictable at the required level of confidence, meaning that irrigation guidelines usually provide generalised irrigation water quality limits, and that identification of saline-sodic water as a resource for water limited environments has been limited. Mechanisms, either directly explaining the interaction of specificity factors, or providing an integration of these effects, are required for meaningful prediction.

Bennett and Raine (2012) demonstrated that the C_{TH} was soil-specific with significant differences occurring within soils of the same order and textural class, without an apparent relationships between the C_{TH} and soil properties such as organic matter, clay content and the clay-cation ratio. Marchuk et al. (2013a) demonstrated that the charge on soil and organic matter, as measured by cation exchange capacity (CEC), does not reflect the actual charge allowed for hydration interactions, due to the destructive nature of CEC measurement methods. They proposed that the net negative charge, measured as the electrophoretic mobility of clay particles (zeta potential; ζ), provided a measure of the actual charge available for hydration interactions. Consequently, it was shown that the net negative charge was determined by distinct clay mineral and

organic matter associations, as well as changes in soil chemistry, and caused the soil-specific occurrence of the C_{TH} (Marchuk et al. 2013a). While the net negative charge explained conceptually why the soil-specific result is obtained, it did not allow prediction of the C_{TH}. Previous research has demonstrated ζ as important in predicting the tendency for the soil colloids to disperse (Chorom & Rengasamy 1995; Chorom et al. 1994; Marchuk & Rengasamy 2011). Therefore, the application of net negative charge to disaggregation processes (intra- and inter- crystalline swelling), prior to clay dispersion and resulting in a reduction of saturated hydraulic conductivity (rK_{sat}), may provide insights towards C_{TH} prediction.

The swelling pressure at the clay domain scale is related to the charge density at the boundary between the Stern layer and DDL, which is the slipping plane (also referred to as the Gouy plane).

Surface density of charge at this point defines the electric potential, and from this along with electrolyte concentration/type and surface separation the swelling pressures within the domain can be calculated (Quirk 2001). The electrical potential at this plane can be measured as the electrophoretic mobility (ζ) and for a clay particle defines the net negative charge (Molina 2013). As the resultant pressure within the clay domain is closely related to the Stern layer charge, we should expect clay ζ to be closely related to the rK_{sat} for a given soil and a function of the EC and SAR at a given system pH. This work tests the hypothesis that ζ is a function of EC and SAR for a given pH and that such relationship is closely related to observed rK_{sat}.

7.2 Methods and materials

7.2.1 Soil selection

Three distinctly different soils were selected – a Vertosol, a Kandosol, and a Dermosol from cotton growing areas of southeast Queensland. Soil samples were collected by shovel from a uniform depth to 0.1 m, air-dried and sieved to pass a 2 mm size. The Kandosol was selected due to its very low clay content, and the Dermosol due to the presence of oxides, in comparison to the Vertosol soil. Soil soluble and exchangeable cations (Rayment & Lyons 2011), turbidity, clay content, water dispersible clay, and zeta potential of the dispersed clays are presented in Table 7.1.

Electrical conductivity, and pH, using 1:5 soil/ deionised water (DW) solutions were measured in a Radiometer analytical ION 450 Meter lab. Exchangeable and soluble

cations were determined on a Perkin Elmer NexIon -ICP MS (Inductively Coupled Plasma – Atomic Emission Spectrometer). For exchangeable cations, the soluble cations were washed with deionised water, centrifuged for 30 min, decanted and analysed to calculate SAR. The soils were then extracted with 0.5M NH_4Cl of pH adjusted to 7.2 and 8.2 depending of respective pH (Marchuk & Rengasamy 2012).

Table 7.1. Initial properties of the soils selected for analysis. The soils were chosen due to their varying physical and chemical properties. Within this table the abbreviations represent; EC- Electrical conductivity, TCC – Total cation concentration, SAR – Sodium absorption ratio, CROSS – Cation Ratio of soil structural stability, ESP – Exchangeable sodium percentage, ECR – Exchangeable Cation Ration, CEC – Cation exchange capacity

Soil		Vertosol	Kandosol	Dermosol
pH		7.95	7.49	8.44
EC (ds/m)	dS/M	0.13	0.04	0.96
Organic matter	%	1.02	0.69	1.56
	Na	1.73	0.08	4.66
Soluble Cations	Mg	0.26	0.07	0.71
(meq/L)	K	0.08	0.21	0.45
	Ca	0.26	0.16	3.74
TCC	meq/L	2.33	0.52	9.57
	Na	0.94	0.01	0.14
Exchangeable Cations	Mg	13.70	0.76	1.72
(Meq/100g)	K	1.00	0.61	0.82
	Ca	20.87	2.04	10.67
CEC		36.51	3.41	13.35
SAR		3.36	0.23	3.13
CROSS		3.86	0.61	3.41
ESP	%	2.57	0.16	1.03
EDP	%	5.49	10.86	4.92
Texture	Australian classification	Clay	sandy loam	silty clay loam
Clay content	%	60	12	23
Water-dispersible clay	%	52	8	11
Zeta Potential		-29	-33	-19
Turbidity (NTU)	Spontaneous	124	460	122
	Mechanical	1566	1290	1200

In order to improve the identification of the mineralogical composition of the soils by XRD analysis, clay fractions were separated by sedimentation (Jackson 2005) as described in chapter 3.1 (Table 7.2). There were marked differences in soil physico-chemical and mineralogical properties of the three soils used in the present study (Table 7.1 and Table 7.2).

Table 7.2. Mineralogical composition of clays (%) from XRD analysis

Soil	Montmorillonite	Kaolinite	Anatase	Hematite	Quartz
Soil 3	72	7	3	1	17
Soil 6	1	29	0	0	63
Soil 7	13	34	0	0	53

7.2.2 Experimental design

The experimental design involved two approaches: 1) assessment of reduction in saturated hydraulic conductivity (rK_{sat}) and 2) assessment of net negative charge (ζ) associated with rK_{sat}. However, assessment of ζ required destruction of soil cores, which would have introduced substantial error in rK_{sat} measurement and required destruction of leaching cores. For this reason, the rK_{sat} was determined using the method of Ezlit et al. (2013) and a second experiment was run to determine ζ on individual cores.

For each soil, 45 cores were prepared to a height of five cm. Each core was contained in PVC tube (10 cm length, 4.5 cm internal diameter) with No. 1 filter paper (42.5 mm) placed at the base of the soil core and the core retained at the base by a plastic mesh. A subsample of 100 g of soil was weighed and transferred into these columns. A bulk density specific to each soil was obtained by dropping each core assembly from 5 cm height three times and then averaging the results. Cores were then repacked to 5 cm thickness to the average bulk density. Another filter paper was placed on the top of each soil column to avoid soil disturbance.

Soil cores were initially wet from the bottom using capillary action under a -40 mm hydraulic head with the head increased to 0 mm (saturation) at a rate of 10 mm hydraulic head/h with $CaCl_2$ (EC 2, SAR 0) solution. At saturation, the pre-treatment was allowed to equilibrate for 12 hours. Following the pre-treatment, the columns were placed into Buchner funnels and allowed to drain. The flow of the water was controlled using a Mariotte bottle with a 5 mm ponded hydraulic head. The pre-treatment solution was applied to all the cores and run to steady state. At this point ≈1.0 g of soil was carefully removed from the surface of each core to obtain a ζ of the pre-treatment.

Each of the 45 cores was then assigned a SAR (1 to ∞) and EC (0.5, 1, 2, 4, and 8 dS/m) treatment solution; there were 9 SAR level per EC (Table 7.3). The treatment solutions were allowed to infiltrate, as per the pre-treatment solution, until steady state was achieved. The columns were subsequently oven dried at 45 C for 48 h, and carefully ground to pass through a 2 mm sieve for further analysis.

7.2.3 Determination of net negative charge

The net negative charge was determine as the zeta potential (ζ) of the samples and was measured with a Malvern Zetasizer using a method modified from that described in Marchuk and Rengasamy (2012). The ζ was determined from aggregated soil systems rather than from manipulated clay suspensions. Measurements of the samples were taken in the solution they were equilibrated to rather than deionised water; i.e. where rK_{sat} was determined at EC=X, the ζ was determined in solution at EC=X. Once soil cores were equilibrated with the desired irrigation solution, a soil sample was taken near the percolation surface and subject to air-drying. A 1:5 soil:solution ratio was used to obtain the ζ reading. Analysis occurred at a constant temperature (22 ^{0}C) with measurements taken over a run time of 30 s, and final values averaged over nine runs.

Table 7.3. Amounts of NaCl and $CaCl_2$ required for preparation of different EC solutions (0.5, 1, 2, 4 and 8 dS/m)

SAR Curve	*Na (meq/L)*	*Ca (meq/L)*	SAR	*Final TCC (meq/L)*	*SAR Curve*	*Na (meq/L)*	*Ca (meq/L)*	SAR	*Final TCC (meq/L)*
	0	80	0	80		75.00	5.00	47.43	80
	0	40	0	40		37.50	2.50	33.54	40
Pre-Treatment	0	20	0	20	**5**	18.75	1.25	23.72	20
	0	10	0	10		9.37	0.63	16.77	10
	0	5	0	5		4.69	0.31	11.86	5
	30.00	50.00	6.00	80		77.00	3.00	62.87	80
	15.00	25.00	4.24	40		38.50	1.50	44.45	40
1	7.50	12.50	3.00	20	**6**	19.25	0.75	31.43	20
	3.75	6.25	2.12	10		9.62	0.38	22.23	10
	1.87	3.13	1.50	5		4.81	0.19	15.72	5
	50.00	30	12.91	80		78.10	1.90	80.12	80
	25.00	15	9.13	40		39.05	0.95	56.66	40
2	12.50	7.5	6.45	20	**7**	19.52	0.48	40.06	20
	6.25	3.75	4.56	10		9.76	0.24	28.33	10
	3.12	1.875	3.23	5		4.88	0.12	20.03	5
	63.00	17.00	21.61	80		78.80	1.20	101.72	80
	31.50	8.50	15.28	40		39.40	0.60	71.93	40
3	15.75	4.25	10.80	20	**8**	19.70	0.30	50.86	20
	7.87	2.13	7.64	10		9.85	0.15	35.97	10
	3.94	1.06	5.40	5		4.92	0.08	25.43	5
	71.00	9.00	33.47	80		80.00	0	Infinity	80
	35.50	4.50	23.67	40		40.00	0	Infinity	40
4	17.75	2.25	16.73	20	**Infinity**	20.00	0	Infinity	20
	8.87	1.13	11.83	10		10.00	0	Infinity	10
	4.44	0.56	8.37	5		5.00	0	Infinity	5

7.2.4 Statistical analysis and data manipulation

Data were investigated using linear and non-linear regression. TableCurve 3D (SYSTAT Software Inc. 2002) was used to fit three dimensional surfaces for rK_{sat} and ζ. Pearson's correlation coefficient was used to determine the regression fit to the observed data, while the degrees of freedom R^2 was used to determine that models had not been over-fitted to the data.

7.3 Results and discussion

7.3.1 Net negative charge as a function of electrolyte concentration and exchangeable sodium

The net negative charge (ζ) of the soils, at pH ranging from 7.49 to 8.44, was described by the following equation (Figure 7.1):

$$\zeta = a + be^{EC} + cESP + d\sqrt{ESP} \qquad \text{Equation 7.1}$$

Where *EC* is the electrolyte concentration ($mmol_c/L$), *ESP* is the exchangeable sodium percentage and *a, b, c* and *d* are fitted parameters (Table 7.4), within the boundary of EC=0.5 to 2.0 dS/m and the physical bounds of ESP. The goodness of the fit for the model was very high for all three soils individually and combined, describing 97, 93, 95 and 93% of the observed variation for the Vertosol, Kandosol, Dermosol and combined soils, respectively (Table 7.4); the degrees of freedom adjusted R^2 indicates that the model has not been over-fitted, with observations exceeding 7 times the number of fitted parameters for the model. Based on the level of precision for the model containing all soils, for pH between 7.5 and 8.5, Equation 7.1 can be generalised to:

$$\zeta = 0.452ESP - 7.94\sqrt{ESP} - 478.9e^{EC} - 8.39 \qquad \text{Equation 7.2}$$

The EC term explains <1% of the variation in the model, meaning that the majority of change in the net negative charge can be attributed to increasing Na within the given concentration. Such a result occurs as the effect of EC on soil structure is a physicochemical compression of the diffuse double layer, occurring prior to the Stern layer (Molina 2013; Quirk 2001). Horikawa et al. (1988) demonstrated that the surface potentials of homoionic montmorillonite and illite remained nearly constant for a concentration range of 10^{-4} to $10^{-2}M$. Within the EC term, fitted parameter '*b*' contributes less than 0.1% to the model, but is responsible for the decrease in net

negative charge, for a given ESP, as EC decreases. The net negative charge change prior to ≈0.75 dS/m is more rapid and non-linear, after which it becomes gradual and linear. This indicates that the EC effect on net negative charge is most influential at low EC.

The results of this work occurred within a pH range of 7.5–8.5, which we suggest has effectively removed the effect of EC on net negative charge from the data interpretation. Chorom et al. (1994) and Chorom and Rengasamy (1995) demonstrated that the net negative charge of clays was affected by changes in pH with a linear relationship, but with soil-specific slope of this relationship. Equation 7.2 does not consider pH, and is therefore cautioned against use outside of the pH range it was developed at.

Both the cation ratio of soil stability (CROSS) (Rengasamy & Marchuk 2011) and the exchangeable dispersive percentage (EDP) (Bennett et al. 2016a) were developed to take into account the varying effects of cations with regard to soil aggregation and dispersion. CROSS is considered equivalent to SAR, and EDP equivalent to ESP, in terms of interpreting the value returned; i.e. CROSS=X is equivalent to an SAR of X, and EDP=Y is equivalent to ESP=Y. However, the ionicity concept on which they are based involves the use of a coefficient that varies with soil (Dang et al. Accepted). The extent of this variation is likely to have important effects on the zeta-potential also. Hence, future work should focus on incorporation of the ionicity concept into the above relationship in order to utilise EDP, rather than ESP.

Table 7.4. Model parameters for the net negative charge fitted surface predicted using TableCurve 3D

Model parameters	*Vertsosol*	*Kandosol*	*Dermosol*	*All soils*
a	-6.489	-9.58	-9.112	-8.394
b	-644.211	-464.524	-327.985	-478.907
c	0.457	0.473	0.434	0.452
d	-8.121	-8.267	-7.407	-7.945
R^2	0.97	0.94	0.96	0.93
Adjusted R^2	0.97	0.93	0.95	0.93
Fitted standard error	2.054	2.859	2.043	2.791

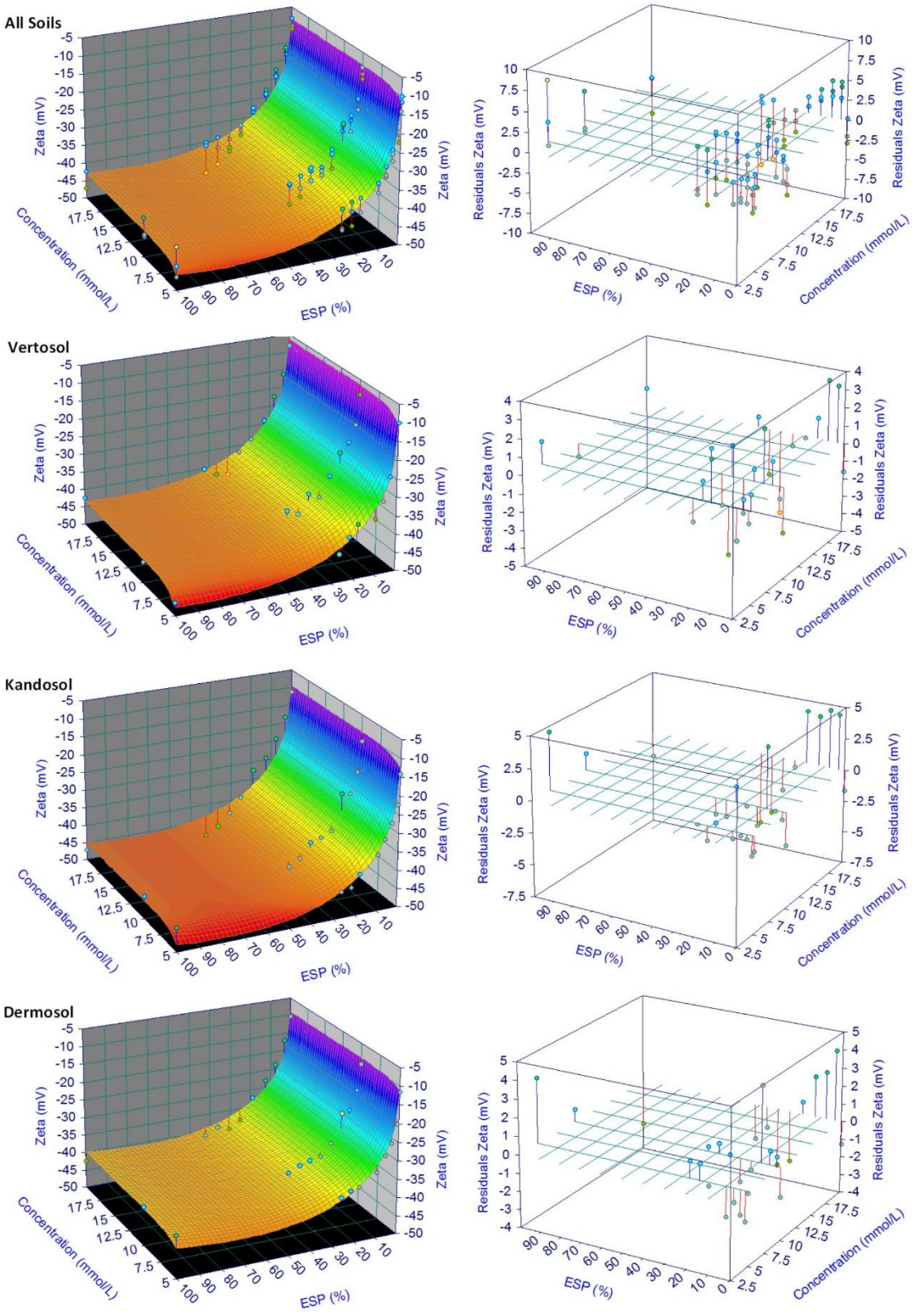

Figure 7.1. Net negative charge of clay (Zeta) as a function of electrolyte concentration and exchangeable sodium percentage (ESP) for the three soils individually and combined, with residuals for net negative charge plotted in the right-hand graphs.

7.3.2 Net negative charge and reduction of saturated hydraulic conductivity

The net negative charge was very highly, and linearly, related to rK_{sat} for the three soils (Figure 7.2). However, the slope of the relationship varied extensively between the three soils, which is directly related to the rK_{sat} for each of the soils transitioning from a pure Ca soil-solution system to a pure Na soil-solution system. In contrast to Figure 7.1, the EC has significant effect on the rK_{sat}, which is due to the compression of the DDL in high salinity soil-solution. Aydin et al. (2004) concluded that K_{sat} is sensitive to ζ, but were unable to predict K_{sat} from their ζ data. Our results support this conclusion, and further allows the prediction of K_{sat} from the ζ data for the individual soils. However, it is clear that prediction between the three soil types is not possible.

The Kandosol soil was selected due to its very low clay content, while the Dermosol was known to have oxides existing within it. While it is not possible from our data to conclusively determine statistical differences between the three soils in terms of mechanisms, we suggest that these features are responsible for lower rK_{sat} at ESP≈100. McNeal (1968) and Frenkel et al. (1978) both showed that for a given ESP and EC the rK_{sat} was greater as clay content increased, meaning higher clay content soils are more susceptible to increase in Na or decrease in EC. McNeal (1968), Deshpande et al. (1964) and El-Swaify (1973) all demonstrated that soils containing iron and aluminium oxides were more stable than where those oxides where chemically removed. Using the definition of C_{TH} occurring at rK_{sat}=20%, prediction of the ζ yields -17, -35 and -23 mV for the Vertosol, Kandosol and Dermosol, respectively. These data do not support occurrence of the C_{TH} at a common ζ, but we note the data for such assessment is limited. Interestingly, the Kandosol net negative charge of -34 mV suggests that C_{TH} exists at a point where dispersion has already occurred (ζ<-30 mV), while for the Vertosol and Dermosol the C_{TH} is associated with a stable soil aggregate system. Such a result does support the findings of McNeal (1968) and Frenkel et al. (1978) that a low clay content soil system can be expected to have less K_{sat} reduction. These data and the literature cited support further investigation of the relationship between net negative charge and rK_{sat} on this basis. Such investigation may reveal important insights for the prediction of rK_{sat} from ζ on a universal basis.

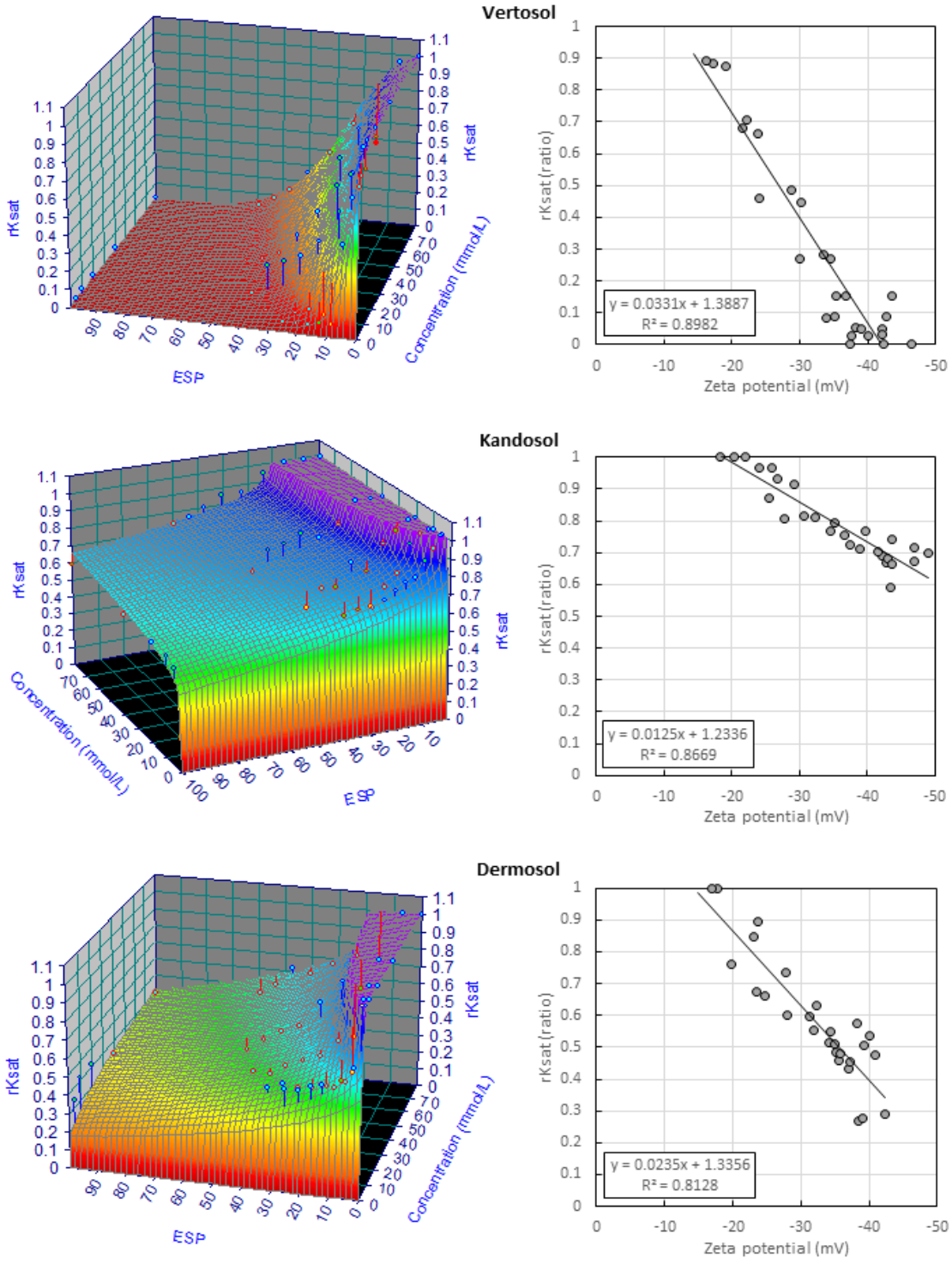

Figure 7.2. The relationship between net negative charge (zeta potential) and the reduction in saturated hydraulic conductivity (rK_{sat}), in comparison with rK_{sat} as a function of electrolyte concentration ($mmol_c/L$) and the exchangeable sodium percentage (ESP), for the three soils.

7.4 Conclusion

This work confirmed the hypothesis that ζ is a function of EC and SAR for a given pH and ζ was very closely related to observed rK_{sat}. The EC of the soil-solution was

confirmed as having a much lower effect on the net negative charge than Na, with a general equation for determination ζ from ESP and EC obtained for the three soils at pH 7.5–8.5. Net negative charge was able to be predicted for a soil from rK_{sat}, but predictions between soils were not possible due to differences between the rK_{sat} in response to approaching a pure Na soil-solution system. It was hypothesised that further investigation on the effect of clay content, sesquioxide occurrence and ζ on rK_{sat} should result in prediction of rK_{sat} from ζ.

7.5 References

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8 General discussion, conclusion and future research directions

8.1 General Discussion

In the present study, the premise of using marginal quality saline-sodic water for irrigation has been well-established and shown to have potential. This work also identifies the strong need for alternative resources for irrigation, due to already increasing pressure on freshwater. However, the body of work conducted in this research has identified a number of impediments to the use of this water with reference to the soil-specific response, the methodology used to determine the suitability of the water, the presence of Mg and K, and the mechanisms controlling the soil response.

The purpose of this chapter is to provide general discussion on the predication of the soil response to a given water quality, the cost-effective approaches that can be undertaken to minimise cost in regards to C_{TH} and the impact that the presence of K and Mg. This chapter has a focus on the key findings within the context of existing guidelines/regulation and provide a strategic approach to updating these in line with the findings of this work. Finally it aims to provide recommendations for future work based on the findings of this thesis.

8.1.1 Guidelines used to determine suitability of a given water quality

8.1.1.1 *Current irrigation water quality guidelines*

There are many different guidelines, created from water quality parameters stemming from different sources, to ensure that MQSS quality water can be used safely and productively (World Health Organization 2006). However, it is important to choose the correct soil, crop, and irrigation management strategies (World Health Organization 2006) to ensure that highest possible agricultural productivity is achieved. To be able to transform reclaimed water into an economic resource in Australia and New Zealand (ANZECC 2000), the current guidelines are defined as an important component of the National Water Quality Management Strategy.

The ANZECC (2000) guidelines for water quality are currently used as a guide to the appropriate selection of saline-sodic water to maintain soil permeability. The ANZECC (2000) guidelines do not stipulate a reduction in K_{sat} from the stable condition to determine a soil's individual C_{TH}. Instead, they refer the reader to a graph with two curves representing the soil in stable and non-stable conditions to determine

whether or not a water quality is safe for use. To determine if a given water quality will detrimentally impact, the guidelines suggest using the SAR and EC to predict soil structure stability in relation to the irrigation water. The SAR and EC are then imposed onto the threshold electrolyte concentration graphs (Figure 8.1) developed by (DNR 1997). According to these graphs, the values of SAR and EC for a given quality of water for irrigation falling on the right side of the dashed line can be safely used without detrimental impact on soil structure. The values of EC and SAR falling on the left side of the dashed line are likely to have detrimental effect on the soil structure. Those values of EC and SAR falling in between these lines require careful consideration of soil, crop and management. This set of guidelines are designed to be universal, however that makes the approach quite conservative. Coal seam gas (CSG) developments in southern Queensland sought case-by-case amendment to the general guidelines on such basis, with over 200 soils assessed (Bennett et al. 2011a, 2011b; Bennett & Raine 2017; Raine 2010; Raine 2012; Raine & Bennett 2011; Raine 2009, 2011; Raine & Ezlit 2010) using the approach of Ezlit et al. (2013). While CSG associated water required treatment in line with Bennett et al. (2016b), this body of work highlights that a lot of potentially suitable land for irrigation with MQSS water is disregarded due to these guidelines. Additionally, Bennett and Raine (2012) demonstrated that the guidelines failed to recommend against irrigation where detrimental reduction in soil structure would be expected to occur (Figure 8.1(b), Soil 1 and 3). There is therefore a need for the ANZECC (2000) guidelines to be revisited.

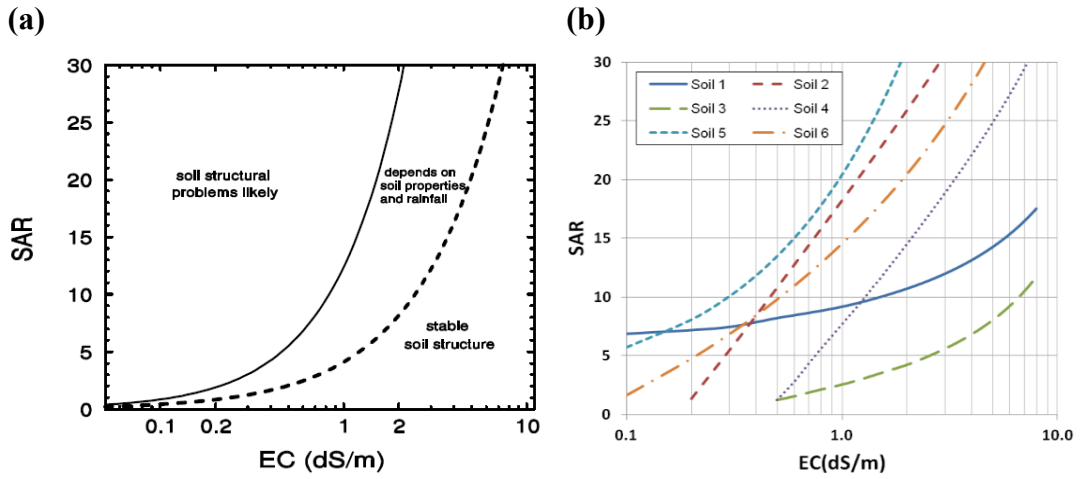

Figure 8.1. Comparison of (a) the relationship between SAR and EC for soil structural stability (TEC) as it appears in ANZECC (2000), modified from DNR (1997); and (b) the TEC (i.e. 20% reduction in Ksat) curves for the three Vertosols (Soils 1, 2 and 6) and three Chromosols (Soils 3–5) soils in Bennett and Raine (2012).

Use of a generalised C_{TH} to create guidelines in regards to irrigation with MQSS water is not suitable, unless such general guidelines protect against the majority of the soils. Additionally, the use of guidelines as opposed to regulation might be questioned. The Queensland Government (Department of Environment and Heritage Protection, 2014) have stipulated beneficial use of Coal Seam (CS) water can be achieved via irrigation, but that this can only occur where such water can be demonstrated to not cause undue environmental harm, even with treatment such as offsetting Na concentration with Ca sources, and/or use of reverse osmosis. The fact the CSG industry is regulated, while agriculture is not, given the difference in land mass between the two industries, is curious. Given the essentially irreversible nature of soil dispersion in terms of its impact on soil infiltration, and that we have known about C_{TH} ramifications since Quirk and Schofield (1955) pioneering paper, it would seem prudent to take steps to protect the land resource. The cost of C_{TH} determination is probably the prohibitive factor of creating regulation in general agriculture (this is discussed further in a subsequent section), but should not be used as a reason in the current era where automation technology has become inexpensive and sophisticated. The body of work in this thesis has further highlighted the extent of structural decline that might occur where MQSS water is mismanaged or applied to soil not capable of receiving it. Therefore, guidelines and/or regulations regarding the use of MQSS water need to be designed with minimisation of harm to the soil resource as the principal focus.

8.1.1.2 *Design of soil specific guidelines*

The implications of current guidelines highlighted in the previous section impacts on farmers' decisions to use marginal quality water in two ways: (i) farmers may use a certain water quality assuming its suitability for their soils based on the guidelines and could have resultant damage to their soils, and/or (ii) farmer may not use a water quality, apprehensive of the potential damage to their soils, preventing marginal quality water from becoming a strategic recourse. It is therefore, necessary for marginal quality water to be considered on a soil-specific basis as a function of the soil response and the water quality, rather than as a single prescriptive guideline. Where soil-specific response is directly tested for the guidelines become redundant as the C_{TH} identified by direct measurement is now the safe operating guideline for that soil. Hence, it is recommended that water quality limits potentially even more conservative than those in the ANZECC (2000) guideline be used as a general limit, with the option

for amendment to this where the C_{TH} of a soil is known for the particular irrigation zone. Such approach has been the basis of the approach to regulating the CSG industry and should be considered appropriate to land application of MQSS water generally.

In terms of the use of MQSS water for land application, there are a number of pertinent questions that need to be answered in order to inform water quality limits:

1. What level of spatial scrutiny is required given the fact we know C_{TH} is soil-specific even within the same soil order?
2. What defines 'undue' soil structural degradation?
3. What percent reduction in K_{sat} should water quality limits be based on?
4. Can water quality exceed safe limits, even beyond the C_{TH} or other identified limit, provided land treatment is applied?
5. What salinity threshold is acceptable given that salinity has a positive effect on soil structure, but is generally negative in terms of crop production?
6. Should water quality limits apply uniformly across Australia, or should limits be more stringent where freshwater resources (including rainfall) are more abundant, and be less stringent in highly water limited environments?

8.1.1.2.1 Spatial heterogeneity

Within this research, 12 diverse soils were examined, with distinct C_{TH} curves and, therefore, different responses to a given MQSS water. Furthermore, another four soils were analysed in terms of both Na and K as the dominant monovalent ion in solution, with C_{TH} soil specific for both circumstances and between soils. This soil-specific result supports the findings in literature (Bennett & Raine 2012; Bennett et al. 2016b; Bennett & Warren 2015; de Menezes et al. 2014; Ezlit et al. 2013; Marchuk & Rengasamy 2012; McNeal & Coleman 1966; Quirk 2001; Raine et al. 2007; Shainberg & Letey 1984), but not evident in the literature is any indication of the spatial heterogeneity of soil response within a soil order. It is likely that digital soil mapping technologies, and the use of proximal sensing technology outputs as covariates of determination, will help inform the level of sampling required. At the very least, the use of suborders (Isbell 2002) as the key determinant would be useful. Selection of a representative site within suborder will remain an issue, but can potentially be informed by less expensive soil coring prior to full C_{TH} analysis. Future work should focus on determining some recommendation, or spatial proxy, for spatial heterogeneity of C_{TH} to inform sampling strategy and frequency.

8.1.1.2.2 Undue soil structural degradation and arbitrary reduction limits

Questions 2 and 3 presented in section 8.1.1.2are inherently interlinked, but still important independent questions. To define undue soil structural degradation, it is important to discuss arbitrary rK_{sat} limits, actual threshold limits and the margin of error associated with these. The C_{TH} concept given in Quirk and Schofield (1955) used an arbitrary rK_{sat} as a threshold measure of a soils susceptibility to water salinity and sodicity. Quirk and Schofield (1955) suggested that this arbitrary rK_{sat} (C_{TH}) to be a 10% reduction from the stable condition, where the stable condition was a perceived state of potential minima. McNeal and Coleman (1966) later proposed a 25% rK_{sat}. Shainberg and Letey (1984) discussed that the error associated with rK_{sat} exceeded ±10% and stipulated that field conditions were more resilient than laboratory conditions, going on to suggest that a 50% rK_{sat} should be used as the C_{TH}. Putting aside the discussion of appropriate limits for now, this clearly insinuates that the C_{TH}, as defined above, is really an arbitrary and measureable reduction whereby its limit needs to be informed by the error in the measurement method.

There is no true discrete point between the soils's aggregated and dispersed state. The clay domain concept (Quirk & Aylmore 1971) states that clays can swell internal to the crystalline structure where crystalline hydration is allowed (smectites) and can further swell between the individual clay plates that make up the domain, due to a diffuse double layer developing. The point where the clay platelets disassociate is the point of dispersion, but is governed by net negative charge and the size of the clay plates, amongst other mechanisms. Where the net negative charge is anything but zero, then the size of the clay plates affecting the charge density and thermal motion will control the actual point that disassociation occurs. As the size of clay domains will differ within a soil, so too will the point of dispersion of each of these. Under saturated conditions, Quirk and Schofield (1955) defined the C_{TU} as the point where dispersed clay was first observed in leachate, and this was later defined to be the average physicochemical threshold of the aggregate-dispersion boundary. The C_{TH} as an arbitrary rK_{sat} was intended by Quirk and Schofield (1955) to occur at an EC less than that at the C_{TU} resulting in a safety factor proximal to four. This essentially provides a buffer for measurement methodological error, spatial variation, dilution effects, and the potential for management mistakes (Quirk 2001). To that end, any definition of 'undue' soil structural degradation should take into account these practical limits. It is

also evident that an arbitrary reduction in K_{sat} is more prudent in terms of managing environmental harm, rather than the use of the aggregate-dispersion boundary threshold suggested by some recent literature (e.g. Rengasamy et al. 2016).

The ANZECC (2000) guidelines do not stipulate a reduction in K_{sat} from the stable condition to determine a soil's individual C_{TH}. de Menezes et al. (2014) discuss that for soils with an initially high saturated conductivity, reduction in K_{sat} beyond 20% might actually be beneficial for soil water retention in certain situations, limiting rapid recharge of groundwater and retaining further water in the root-zone. Similarly, Shainberg and Letey (1984) suggested that tolerance to reduction given the initial absolute K_{sat} should be taken into account regarding the setting of rK_{sat} limits for soils. The Kandosol in Chapter 0 only underwent a 40–50% reduction in K_{sat} where a pure Na solution was irrigated, however was clearly dispersive in terms of the net negative charge. However, it is suggested that this be an exception to the rule as a general guideline variation, rather than an explicit water quality limit based on texture.

This work then contends that to answer the question of undue soil structural degradation, the C_{TU} should not be breached, as tolerable should be practically defined as minimising environmental harm, for the general case. If the rK_{sat} is less than observed at the C_{TU} then the change in saturated hydraulic conductivity is theoretically reversible (Quirk & Aylmore 1971; Quirk & Murray 1991; Quirk & Schofield 1955), although the extent of this reversibility is not currently known for the soils used in this work. The observed rK_{sat} of the five soils in Chapter 0 confirmed that rK_{sat} at the C_{TU}>>rK_{sat} at the C_{TH}, ranging between 43–55, 42–46, 55–78, 65–75, and 33–52% for Soils 1 through 5, respectively. For three of these five soils, the recommendation from Shainberg and Letey (1984) of a rK_{sat}=50%=C_{TH} would result in undue soil structural degradation. Where rK_{sat}=20%=C_{TH} undue soil structural degradation (i.e. breach of C_{TU}) did not occur for any of the five soils. Based on this, it would appear that a general guideline using C_{TH}=20% reduction in K_{sat} is appropriate and that amendment to this for a soil can only be made where C_{TU} is known.

8.1.1.2.3 Use of water quality beyond safe limits

This work did not directly test whether or not the treatment of soil with an ameliorant could offset the use of water quality poorer than that advised by C_{TH} at rK_{sat}=20%. However, this needs to be considered in the formulation of guidelines and regulations.

The CSG industry has employed this approach under Government regulation in Queensland, Australia (Bennett et al. 2016b), as well as in the Powder River Basin, Wyoming, USA (Johnston et al. 2013; Johnston et al. 2008; King et al. 2004). The general finding of these investigations was that the SAR of irrigation water was able to be offset by land application of gypsum, and that the alkalinity could be addressed via a sulphur source. The extent of effect was clearly a function of application amount and requirement, as well as the dissolution characteristics of the ameliorant used. It is suggested that such allowances should be made as a variation to a general regulation, where C_{TH} has been directly undertaken and justification of solubility efficiency is justified.

8.1.1.2.4 Salinity thresholds considerations for soil and crop

Again, this body of work did not assess the suitability of salinity thresholds for crop establishment against the C_{TH} observations for the soils investigated. However, it is well understood that excessive salt contained within irrigation water may lead to accumulation of soluble salts in the root zone, or if applied above the canopy, accumulation of salts on the plant leaves. Published salinity thresholds are also known to be affected by the method of measurement used to determine them (Tavakkoli et al. 2010; Wehr et al. 2016; Zhang et al. 2011), while different soils may have specific effects on germination (Ma et al. 2015; Tavakkoli et al. 2010). Giles et al. (2014) observed that seedling growth of leucaena decreased by 50% at 4.9 dS/m in a sand culture, which was greater than previous values reported for solution based observation, or petri dish media. Current Australian irrigation salinity limits for irrigation with saline water have approach 4.0 dS/m (Bennett & Raine 2017), with numerous species having been identified as suitable for growth at such salinity (Cicchelli et al. 2016; Giles et al. 2014; Pachas et al. 2016; Wehr et al. 2016). In terms of salinity limits, a pertinent point will remain the requirement for management of stored salts within the root zone via a leaching fraction (Shaw & Thorburn 1985), which is a current consideration of the ANZECC (2000) guidelines and should always remain so. Any variation to salinity limits will need to consider the fresh-water availability in the regions, versus production demand and future fresh-water availability likelihood; i.e. will a variation to a general limit result in environmental change that limits the potential of future production options, given the likelihood of future resource availability?

8.1.1.2.5 Uniformity of spatial application of water quality limits

Whether or not water quality limits apply uniformly across Australia, or should be more stringent where freshwater resources (including rainfall) are more abundant, and less stringent in highly water limited environments is well beyond the scope of this thesis. However, it is an extremely important consideration as it will affect the future production potential of the land resource. This was briefly discussed in the above section, where it was identified that environmental harm in the short-term must be weighed against future requirements and resource availability. It is impossible to know these explicitly, but failure to consider the question at all is likely to result in unexpected impacts in the long-term. Qadir and Oster (2004) and Qadir et al. (2007b) present good discussion of this precise issue, with the focus on the use of MQSS water in water limited environments where fresh water resources are unlikely to be made available in the foreseeable future.

8.1.2 Inclusion of cations other than sodium in threshold electrolyte concentration analyses

Traditional approaches to measuring C_{TH} utilise SAR and ESP, and do not include the potential effects of K and Mg. Recent advances in the variable effects of cations on dispersion and flocculation (Arienzo et al. 2009; Rengasamy & Marchuk 2011; Smith et al. 2015) demonstrate that incorporation of K and Mg should be considered in terms of assessing soil structural condition in response to water quality and, therefore, C_{TH}. For this reason, Marchuk and Rengasamy (2012) and Rengasamy and Marchuk (2011) investigated C_{TH} and dispersive potential in relation to CROSS to include the effects of the full cation suite as a direct measure of clay dispersion in water. Bennett et al. (2016a) also suggest that EDP is equivalent to ESP, and that the inclusion of K in this index significantly improved the explanation of variability in dispersed clay. The premise of Chapter 5 was to use Bennett et al. (2016a) proposed EDP, instead of ESP in the disaggregation model to allow for incorporation of K. However, the work in this thesis has highlighted that a universal coefficient was not an accurate approach, which supports the findings of Smith et al. (2015). Additionally, while it was found that the coefficient appeared to vary between soils, it also appeared to vary depending on the concentration of K in the percolating solution, which could indicate processes other than dispersion. The conclusion drawn against this work was that use of universal, or directly measured and generalised, coefficients of equivalence for K was a suitable

approach as in all cases the model was conservatively wrong; i.e. it did not result in further undue soil structural degradation. However, the approach requires further investigation and optimisation.

Dispersive potential (P_{DIS}) (Rengasamy & Olsson 1991) was designed as an alternative to the C_{TH} approach (Ezlit et al. 2013), based on the difference between osmotic pressure at the threshold point (P_{TEC}) and the pressure in the soil solution concentration to achieve complete flocculation (P_{SOL}) (Marchuk & Rengasamy 2012; Rengasamy & Sumner 1998). While dispersive potential was suggested as an alternate to the C_{TH} method in determining the suitability of a MQSS water for irrigation, designed to eliminate the soil-specific variation in determining the threshold point and allow inclusion of K and Mg directly, the work in this thesis has demonstrated that its use for non-dispersive soils is problematic. Additionally, it still relies on coefficients of equivalence derived from the ionicity concept. In order for the method to provide results that informed the C_{TU} the equilibrated soil samples required rapid dilution and processing in distilled water, which extended the time taken to complete the method and severely limited the functional domain of observations in terms of CROSS. The relationship between C_{TH} and C_{TU} was also demonstrated as inconsistent between soils in terms of a standard safety factor. Thus, the use of dispersive potential to combine the effects of K and Mg into C_{TH} analyses is not recommended.

Smith et al. (2015) clearly demonstrated that the coefficients of equivalence are able to be optimised to provide a better relationship between CROSS and the extent of dispersed clay. Given the results obtained for K in this thesis, it appears that the first step in including cations other than Na and Ca in C_{TH} is understanding the physical extent of variation of such coefficients of equivalence. This is able to be done mathematically, but should also be confirmed experimentally on a larger range of soils than the four presented in Rengasamy and Sumner (1998). There is also a need to better understand the specific effect of Mg, which was beyond the scope of this thesis.

8.1.3 Prediction of soil response to a given water quality

Ezlit et al. (2013) modified the McNeal clay swelling model (McNeal 1968) providing a semi-empirical model for determination of the C_{TH}. However, use of the current models is hindered by the soil-specific response to MQSS water. This thesis sought to better understand the mechanisms controlling the soil-specific response of a soil to a

given water quality. There remains a lack of clarity with regards to the implementing the mechanisms suggested to be controlling the soil specific response to a given water quality with regard to their significance in the prediction of C_{TH} and inclusion in a predictive model. The mechanisms suggested to have an impact on C_{TH} are clay content (Frenkel et al. 1978; Goldberg et al. 1991; McNeal & Coleman 1966) and type/amount of organic matter (Murphy 2015; Nelson & Oades 1998). Bennett et al. (Submitted), using 30 soils found that there was no direct overriding relationship between any of these and the resultant C_{TH}, except for clay content. The present study confirmed that clay content has an important effect on the resultant rK_{sat} for a given water quality, supporting literature (Frenkel et al. 1978; McNeal 1968; Shainberg & Letey 1984), but further demonstrated that net negative charge was more strongly associated with rK_{sat}. In fact, it was apparent that clay content and sesquioxide presence affect the slope of the relationship between net negative charges, but did not affect the strength of the relationship. This result does require further validation, but provides promising ground on which to work towards direct C_{TH} prediction.

A crucial mechanism that still lacks quantifiable impact with regard to the soil-specific effect is clay mineralogy. Bennett et al. (Submitted) found that soil pH and the semi-quantitative amount of kaolinite helped explained some of the variance in the soil specific response to C_{TH}. The charge systems of kaolinites is dominated by protonation-deprotonation processes, which explains the interaction between pH and Kaolinite (Chorom et al. 1994; Churchman & Oades 1995). Quirk (2001) and Rengasamy et al. (2016) and Bennett et al. (Submitted) found that CEC cannot explain the soil-specific response to a MQSS water and that net negative charge was a better determinant, which appeared to account for clay mineralogy influence, but still appeared to be influenced by the clay mineralogy. Hence, further emphasis on quantifying clay mineralogy effect in relation to net negative charge should provide valuable information for C_{TH} prediction.

8.1.4 Cost-effective approaches to threshold electrolyte concentration analysis

The current method for determining C_{TH} involves conducting a full hydraulic conductivity analysis in the laboratory using a pre-treatment solution ($CaCl_2$) with 9 subsequent solutions transition towards a pure Na system. Each solution is required to be run to steady state, which generally occurs after at least 7 pore volumes, and results in between 2 to 3 weeks of analyses for a single soil depending on smectite content

and clay content. The average cost for 200 analyses undertaken manually between 2010 and 2012 was $3000 per soil (J. McL. Bennett Pers. Comm.). As this thesis has not presented a pedotransfer function capable of predicting C_{TH} it is valuable to briefly present some approaches that may prove cost-effective for C_{TH} determination in the short-term.

8.1.4.1.1 Simplified direct measurement

A full C_{TH} analysis provides a C_{TH} curve over EC 0.5–8.0 dS/m, requiring 5 soil cores to be run simultaneously (Ezlit et al. 2013). However, it is unlikely that the on-farm water quality is that variable. Additionally, it is more likely that SAR can be managed on-farm than EC. Where EC is able to be diluted with a freshwater resource, the resulting EC solution can be planed for. That is, the C_{TH} methodology could be undertaken using a single soil core at a specified EC and the C_{TH} simply calculated in 2 dimensions (rK_{sat}, SAR) for the given EC. Apparatus, preparation and implementation of the method for a single core is much simpler than undertaking the full analysis.

8.1.4.1.2 Development of automation equipment

Automated falling head apparatus for the determination of K_{sat} have been developed by German company UMS, although these would not be suitable for automated measurement of K_{sat} in off the shelf format. They operate on a pressure transducer system where by the rate of change in the falling head provides an equivalent and calculable change in pressure that can subsequently be related to volume loss over time. Such a principal could be manipulated for a constant head device as well using either pressure transducers, or sensing technology to measure change in head height. Designing the system to identify steady state conditions as a function of head change and outflow EC, would also allow for automated change from one solution to the next. The number of solutions for automated change simply being a function of the allowable space, which is a further function of the pore volume of the soil core in question. Such a system would decrease the implementation costs to initial preparation of soil cores and the preparation of irrigation solutions. This provides the potential to decrease the time of analysis in terms of laboratory technician time from 73–109 hours to 11 hours, which would reduce the average cost of $3000 to $302–452 on a direct proportional basis.

8.2 General Conclusions

This thesis has clearly demonstrated that MQSS water is suitable as a strategic resource with qualities poorer than Australian guidelines feasible for irrigation production provided soil response is assessed on a case-by-case basis. In order for such water to be utilised strategically, this work has highlighted that there are a number of considerations on both a scientific and regulation level that need to be taken into account to minimise environmental harm. However, where the C_{TH} is adhered to in terms of current definitions (i.e. rK_{sat}=20%) then use of water not exceeding reduction in K_{sat} beyond this could be used immediately with confidence that environmental harm is minimised.

From the topics and themes investigated in this thesis, the following conclusions were drawn:

- Due to there being a soil-specific response, a C_{TH} analysis needs to be undertaken for each soil in order for MQSS water to be used appropriately; a generalised guideline is not appropriate unless it has been constructed to be conservative (accounting for safe irrigation for more than 90% of soil's C_{TH}).
- The use of the laboratory based semi-empirical disaggregation model to provide practical recommendations for field application was validated. The disaggregation model, in terms of rK_{sat} was capable of appropriately predicting the reduction in K_{sat} from previously unirrigated soils for soil pore solution and irrigation solution water qualities obtained from irrigated soils of proximal location. On this basis, the use of C_{TH} is warranted for practical field management and strategic irrigation resource planning.
- The current form of C_{TH} analysis needs improving to include the presence of Mg and K. Incorporation of K directly into the disaggregation model resulted as equivalent to Na based on CROSS coefficients of equivalence tended to exaggerate the observed rK_{sat} of the observed K impact on K_{sat}. However, it was clear that K did result in K_{sat} reduction. On this basis, the use of the disaggregation model with K represented as equivalent to Na on the basis described above results in a conservative prediction and could be used where appreciable K exists in irrigation water, or industry waste water; i.e. it is better to be conservatively incorporated than to suggest it has no effect, which exclusion of it from the model would result in.

- The dispersive potential represents C_{TU} and not C_{TH}, with the relationship between C_{TU} and C_{TH} in consistent between soils in terms of difference in rK_{sat} between these thresholds. This demonstrates that the safety factor ascribed by the use of rK_{sat} at either 10% or 20% is not consistent and therefore needs to be considered in management applications. Thus, dispersive potential was not reliable or efficient for C_{TH} determination of non-dispersive soils equilibrated with an irrigation solution.
- The coefficients of equivalent associated with CROSS were reconfirmed as soil-specific and suitable for optimisation or direct measurement. This is important for soil structural relations in general, not just the C_{TH} concept.
- The use of C_{TU} for management guidelines is not suitable. Application with varying irrigation water qualities is strategically possible if the rK_{sat} chosen as the tolerable reduction is in between that at the C_{TU} and C_{TH}, but would require careful consideration and management.
- Current guidelines surrounding the use of marginal quality water for irrigation need to be updated to reflect changes in both science and the availability of technology. The guidelines must integrate the theory of soil-specific response to a given water quality, the effects of K and Mg, and appropriate reduction values for the rk_{sat}. Creation of such guidelines explicitly was beyond the scope of this thesis.

8.3 Recommendations for future work

Based on the outcomes of the individual chapters and the general discussion, the following future work is recommended:

- The current guidelines in place in regards to MQSS water are outdated, as has been extensively discussed. Direct future work involving government, academia and industry should focus on the development of such guidelines, potentially as regulations, in order to better protect the soil resource and the longevity of production potential. Additionally, a variation exemption to such rules needs to be developed in tandem to allow for better exploitation of marginal water on a strategic basis. The Australian CSG industry has provided good catalyst for such development.
- The current method for C_{TH} analysis is time-consuming and laborious, resulting in it being cost prohibitive. Automating the process should be a focus of future

work in order for the use of guidelines to become cost feasible regulations for industries that seek to use MQSS water for land application.

- The ionicity concept needs to be incorporated into hydraulic conductivity reduction models to provide more suitable predictions of changes in the soil structural system. Reliability of prediction of the extent of effect of K and Mg remains to be investigated in terms of hydraulic conductivity reduction. The coefficients of equivalence should be determined directly for a large set of diverse soils (mineralogically, texturally, and in terms of sequioxides) and subsequently used for development of optimisation techniques.
- A predictive model for C_{TH} is still required, with net negative charge providing a promising avenue for such prediction. Future work needs to focus on how the slope of the net negative charge and rK_{sat} relationship is influenced by easily measureable factors. If such the rate of change of this relationship can be explained, then the primary factors explaining soil-specificity of the C_{TH} will have also been explained. From such a point it should then be possible to develop a pedotransfer function that predicts the C_{TH} based on simply and cheaply determined attributes.

8.4 References

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10 Appendices

10.1 Factors controlling soil structure

The following expands on the fundamental factors controlling soil structural stability, providing an introduction to the key concepts used in this thesis.

10.1.1 Clay mineralogy

There are three main groups of clay minerals, each with its own particular properties: montmorillonite, illite/smectite, and kaolinite clays (Brady & Weil 2002). On the microscopic scale, each of these clays has a different lattice structure, i.e. different building blocks (Churchman et al. 1993), which directly affect the ability of Na to bind to each type.

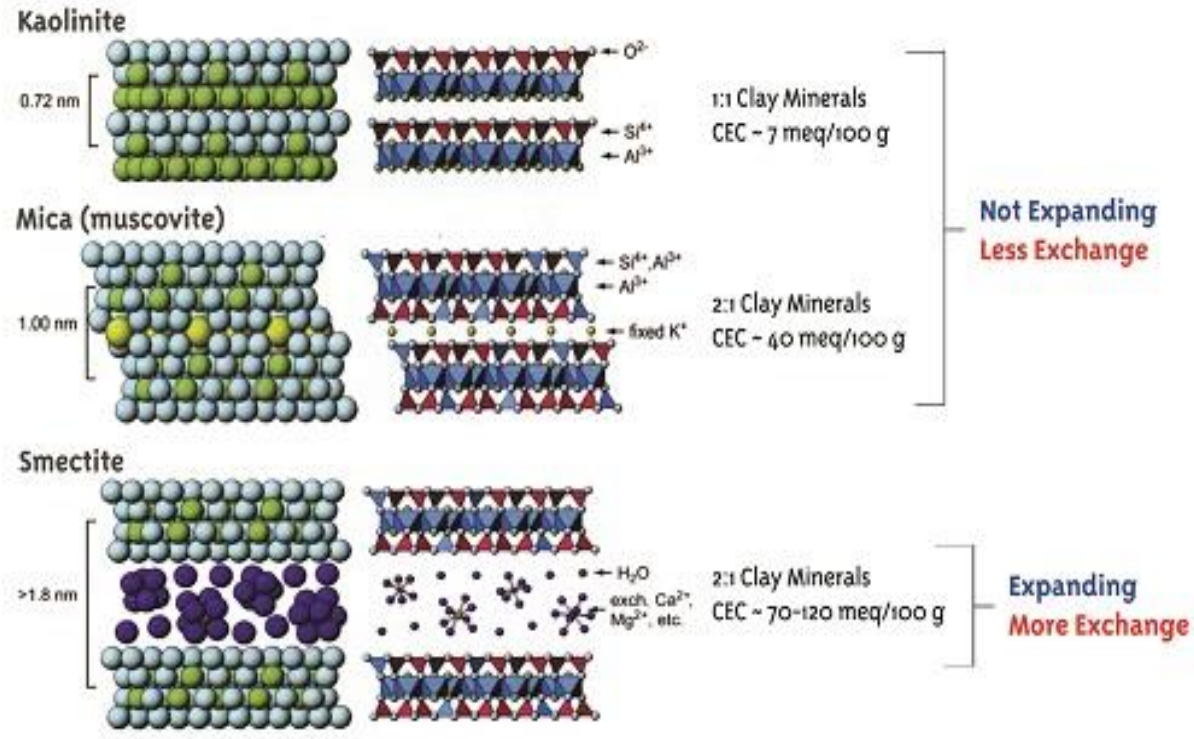

Figure 10.1. Schematic diagram of soil structure of the major types of clays (Soil Science Society of America 2012).

Clay mineralogy influence the specific reaction of soil to Na, determining if the solid phase in contact with the soil solution will lean towards extensive swelling and/or dispersion (Churchman et al. 1993). Extensive swelling can be reduced by replacing exchangeable Na^+ with another cation of smaller hydrated radius or greater valence, as well as by impractically high applications of electrolytes (Churchman et al. 1993; Gardner et al. 1959; Rengasamy 1983). Importantly, this extensive swelling occurs prior to dispersion, suggesting that swelling is somewhat reversible. However, it must

be noted that once the clay domain has dispersed, it does not reform as an aggregate but as a floc (Quirk 2001; Sumner 1999). Thus, soil dispersion is not reversible. The point at which dispersion occurs depends on numerous clay particle characteristics.

Due to the structure of the clay lattices of each clay type, Na has different effects on the permeability of different clay types. The smaller the size of a particle in a given mass of soil, the greater the surface area exposed for adsorption, catalysis, precipitation, microbial colonisation and other surface phenomenon (Brady & Weil 2002).

The silicate clays fall into three subcategories, which are 1:1, 2:1, and 2:1:1 type minerals. A 1:1 clay refers to a clay made with a sheet of octahedral aluminium hydroxide and a tetrahedral sheet. Along with a low surface area, these clays don't tend to expand and have a low CEC. This causes a decrease in the soil aggregate stability. Kaolinite has a good flocculation capacity due to electrostatic charges between platelets (Schofield & Samson 1954). Alternatively the 2:1 clays such as montmorillonites have a two tetrahedral sheets externally with an octahedral sheet in the middle. The surface area and CEC of these clays is relatively high leading to a high amount of aggregation. These clays also tend swell a lot more during the wetting process (Chibowski 2011).

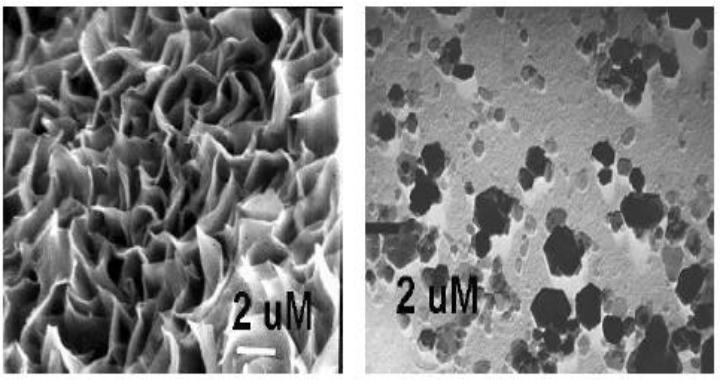

Figure 10.2. Electron micrographs of montmorillonite and Kaolinite showing different surface areas (Marchuk & Rengasamy 2010) (Source: Department of Crop and Soil Environmental Sciences, Virginia Polytechnic Institute and State University).

Kaolinite is quite different to the other clays and is considered to be the least active and it has a low capacity to absorb exchangeable cations at 5-10 milliequivalents of a cation charge per 100g, due to un-terminated bonds on crystal edges. Soils with a presence of illite have a higher cation exchange capacity than kaolinite due to the surface charge. They also have high K^+ fixing capacity. The negative charge resulted from isomorphous substitution of Al^{3+} replacing Si^{4+} in the tetrahedral sheet of illite, is balanced by K^+ predominantly (Grim 1939; Mukherjee 2013; Powrie 2013).

Montmorillinites have low layer charges with cation attraction of nearly 135 milliequivalents.

An excess negative charge on the three basal oxygens and apical oxygen is created in montmorillonite due to substitution of R^{3+} (commonly Al^{3+} and Fe^{3+}) for Si^{4+} in tetrahedral sites. This affects the total charge of the 2:1 layer as well as the local negative charge at the layer surface. Furthermore, an excess negative layer charge is also created by substitution of divalent cations for trivalent cations in octahedral layer. A similar pattern is followed in the soil swelling capacity, with greatest swelling capacity demonstrated by montmorillonite clays and kaolinite clays having the least swelling capacity (Brady & Weil 2002).

Table 10.1. Typical aluminosilicate minerals in the clay fractions of soils (Brady & Weil 2002), particle size data from (Donaldson et al. 1995; Yong & Warkentin 1975)

Mineral	Type	Thickness of cell (Å)	Thickness of clay plate (Å)	Particle diameter (μm)	Surface area		Net negative charge ($cmol_c/kg$)
					External (10^3 m^2/kg)	Internal (10^3 m^2/kg)	
Kaolinite	1:1	7	500-20000	0.3-4	5-30		-1 to -15
Montmorillonite	2:1	9.6	10-80	0.01-0.1	80-150	550-650	-80 to -150
Illite	2:1	10	>30	0.1-0.3 (or larger)	70-175		-10 to -40

The full extent of clay minerology on dispersion is currently unknown. Clay mineralogy of the soil can change the way that a soil would react to different marginal quality waters (Churchman et al. 1993).

10.1.2 Exchangeable cations

10.1.2.1 *Cation hydrated radius and charge*

Presence of charge in cations attracts water molecules and hydrates them (Hillel 2003). Poorest flocculators of clay are cations with a single charge and large hydrated radii. Highly hydrated ions (i.e. Na) with a valence of 1 and a large hydrated radius have a low charge density (Tansel et al. 2006). When those cations are adsorbed on colloid surfaces, they do not effectively counter net negative charges. Consequently, the negatively charged colloid particles repel each other and remain in suspension. The opposite occurs with higher valence cations which have a smaller hydrated radius i.e.

Al^{+3}) (Walworth 2006). The net negative charge of the suspended colloids is completely countered by cations due to their large charge density.

Table 10.2. The cation hydrated radii for the four cations that this thesis mainly focuses on. (Walworth 2006)

Cation	Charges per molecule	Hydrated radius (nm)	Relative flocculating power
Sodium	1	0.79	1.0
Potassium	1	0.53	1.7
Magnesium	2	1.08	27.0
Calcium	2	0.96	43.0

Divalent cations such as Ca^{2+} are attached closer to the colloidal surface due to a stronger attraction to the clay anions (Sumner 1993). Both Ca and Mg are divalent cations; however, due to the smaller hydrated radius, Ca has greater stabilising properties when compared to Mg (Hillel 2003). McNeal (1968) showed that mixed Na–Mg soils developed lower hydraulic conductivity than did Na–Ca soils under similar conditions due to the size of hydrated Mg which is larger than hydrated Ca. Thus, the soil surface tends to absorb more water than where exchangeable Ca is present (McNeal 1968), resulting in weakening of the forces that keep soil particles together. This, in turn decreases the amount of energy to break down soil aggregates (Oster & Schroer 1979; Oster & Shainberg 2001).

10.1.2.2 ***Diffuse double layer***

Diffuse double layer (DDL) is an ionic structure that describes the variation of electric potential near a charged surface such as clay, and behaves as a capacitor (Mojid 2011). A DDL is formed in soil when clay particles are surrounded by a hydrosphere of adsorbed water that contains a thin layer of adsorbed cations (Bennett 2011; Sumner 1992). The adsorbed cations are influenced by electrostatic attraction, but those in the DDL are influenced by two equal but opposing forces i.e. electrostatic attraction and diffusive forces. The clay particles are usually alumina-silicates in which some of the aluminium and silicon ions are replaced by elements with different charge (Sumner 1992). The negatively charged colloidal surface and the positively charged cations in solution form the DDL (Sparks 2003); as shown in Figure 10.3

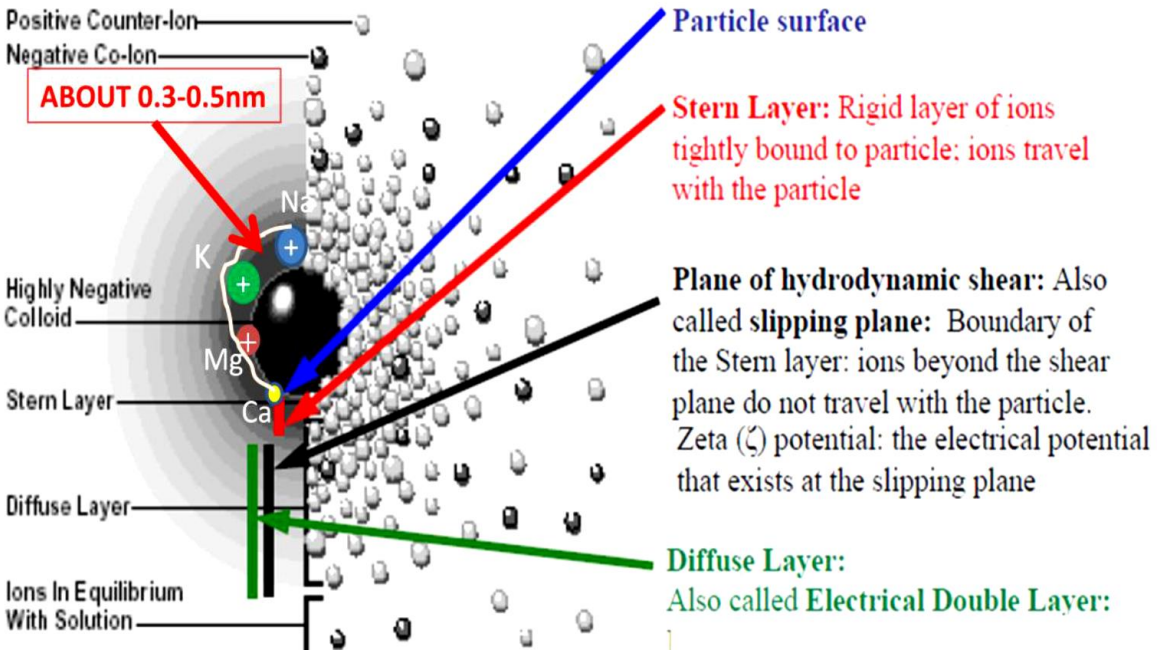

Figure 10.3. The left side of the picture shows the change in charge density around a colloid and the right side shows the distribution of positive and negative charges around the charge colloid. These are two different ways to visualise the Double layer (Marchuk 2013).

The valencies of the ions in solution also play an important role in relation to the size of the DDL. Two variable factors (i) the valency of the cations (i.e. the exchangeable cations), and (ii) the ionic strength (EC) of the soil solution determine the thickness of the DDL. As the valency of cations and/or the ionic strength increases, the width of the DDL decreases. As a result, exchangeable cation concentration decreases exponentially with distance from the negatively charged soil surface (Qadir & Schubert 2002). Ions with a larger hydrated radius are held less strongly than ions with a small radius (Hillel 2003). Hence, Na^+ provides conditions that allow a significant increase in the size of the DDL.

10.1.2.3 *Stern layer*

The stern layer is the layer formed from the counter ions that occur when the positive ions firmly attach to the layer around the surface of the colloid, and exists between the DDL and the clay particle. The stern layer causes a repulsion of the positive ions (Swartzen-Allen & Matijevic 1974). This dynamic equilibrium results in the formation of the diffuse layer of counter ions.

In contrast to the exponential decay of charge in the diffuse layer, the Stern layer has a linear decline in charge with distance (Gregory 1993). The rate of decline, or the

slope of the charge versus distance curve, depends on the capacitance (C1) of this layer, which is further dependent on the total charge and type of ions in this layer (Tan 2010). Beyond the Stern layer, the charge decays as described by the Guoy-Chapman diffuse layer equation (Brown et al. 2016).

One of the major limitations with the Stern model is that it assume that all significant interactions that occur within the diffuse layer are coulombic, it treats the ions as point charges (Hunter 2013). It also assumes that the throughout the double layer the dielectric permittivity is constant. Finally, it also assumes that above the slipping plane the fluid viscosity is constant as shown in Figure 10.4.

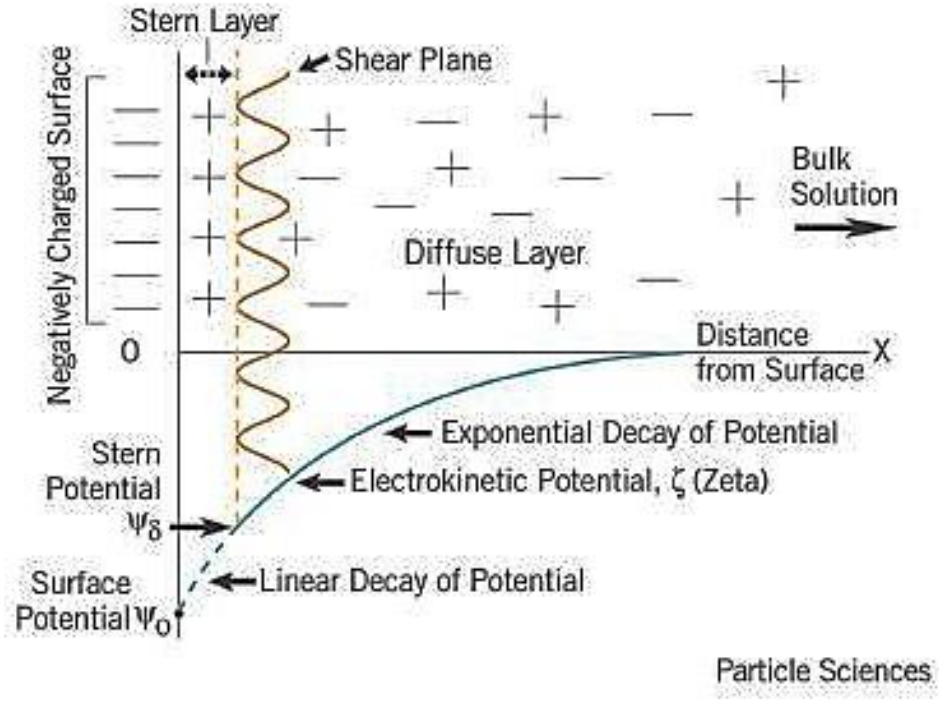

Figure 10.4. A simplified model of the electric double layer at a charged interface in a Aqueous solution demonstrating the different effects of stern layer and diffuse layer (Fairhurst 2013).

Unlike the diffuse layer, the Stern layer is considered to be rigidly attached to the colloid. The stern layer model deals with specific ion sorption. The Stern layer is in the space between the charged particle and the Shear plane (Hunter 2013). Clay surface charge is the electrical potential difference between the inner and outer surface of the dispersed phase in a colloid (Graf & Kappl 2006). Clay surface charge density provides the maximum surface potential. Ions can be adsorbed onto the surface up to a point referred to as the slipping plane, where the ions adsorbed meet the bulk liquid.

Zeta potential is the electrical potential at the slip plane related to the mobility of the particles (Zeta-Meter 1997).

The stern layer exchange sites are also crucial as that is the major determinant of the Gapon exchange constant (Quirk & Marcelja 1997; Sparks 2003). If the Gapon exchange constant is large it indicates that mineral species has a lower charge density and vice versa (Quirk 2001). The size of the swelling pressure that determines the amount of clay platelet separation is influenced by mineral species. A clay net negative charge (zeta potential) that can be used to describe C_{TH} is common between the resultant pressure and the stern layer charge (Bennett et al. Submitted).

10.1.2.3.1 Use of Zeta potential in predicting soil structure

The tendency of the soil colloids to disperse can be assessed by the value of zeta potential (ζ) obtained from electrophoresis experiments (Aydin et al. 2004). Zeta is one of the most fundamental parameter when studying soil stability as it is a measure of the magnitude of the electrostatic or charge repulsion/attraction between particles (Hajnos & Cieśla 2011). It can provide an insight into the causes of dispersion, aggregation or flocculation as well as making it possible to improve the formulation of dispersions, emulsions and suspensions while being simple, fast and cheap (Zadaka et al. 2010).

The zeta potential is a value describing the net electrical charge contained within the region bounded by the slipping plane (Figure 10.4), and depends on the location of that plane. The difference between zeta potential and the stern potential is the different locations at which they are placed (Hunter 2013). Zeta potential at times is regarded as the only proper available path for the characterisation of double layer properties. The net charge depends on a unique association between organic matter, clay mineralogy, and EC and soil pH (Marchuk et al. 2013a).

Electrophoresis phenomenon describes the movement of a charged particle with a fixed velocity in a voltage field (Salman et al. 2007). The slipping plane is the boundary between a moving particle and the liquid, and is the point where the Stern layer and the diffuse layer meet. The Stern layer is rigidly attached to the colloid, while the diffuse layer is not (Salman et al. 2007). Electrical potential at this juncture is called the zeta potential and can be quantified (Zeta-Meter 1997). This involves tracking the

colloidal particles through a microscope during their migration in a voltage field (Zeta-Meter 1997).

A high zeta potential (more negative than -30 mV) indicates high soil clay dispersion (Table 10.3). A low zeta potential is an indicator of when the forces will exceed the repulsion causing flocculation and a break in the dispersion (Hunter 2013). Colloids with high zeta potential (negative or positive) are electrically stabilized, leading to dispersion, while colloids with low zeta potentials tend to coagulate or flocculate (Marchuk et al. 2013a).

Table 10.3. Zeta potential in terms of clay behaviour (O'Brien 1990)

Zeta potential [mV]	Stability behaviour of the colloid	Clay Behaviour
from 0 to ±5,	Rapid coagulation or flocculation	Flocculation
from ±10 to ±30	Incipient instability	Low flocculation
from ±30 to ±40	Moderate stability	Moderate dispersion
more than ±61	Excellent stability	High dispersion

Zeta potential is important in predicting the tendency for the soil colloids to disperse (Shainberg & Letey 1984). Zeta potential has the ability to become a major tool in water quality analysis as the possibility of using net negative charge theory to predict the C_{TH} gains more ground (Marchuk et al. 2013a). The specific adsorption of ions onto a particle surface, even at low concentrations, can have a dramatic effect on the zeta potential of the particle dispersion () (Shainberg & Letey 1984). In some cases, specific ion adsorption can lead to charge reversal of the surface (Malvern Instruments 2012).

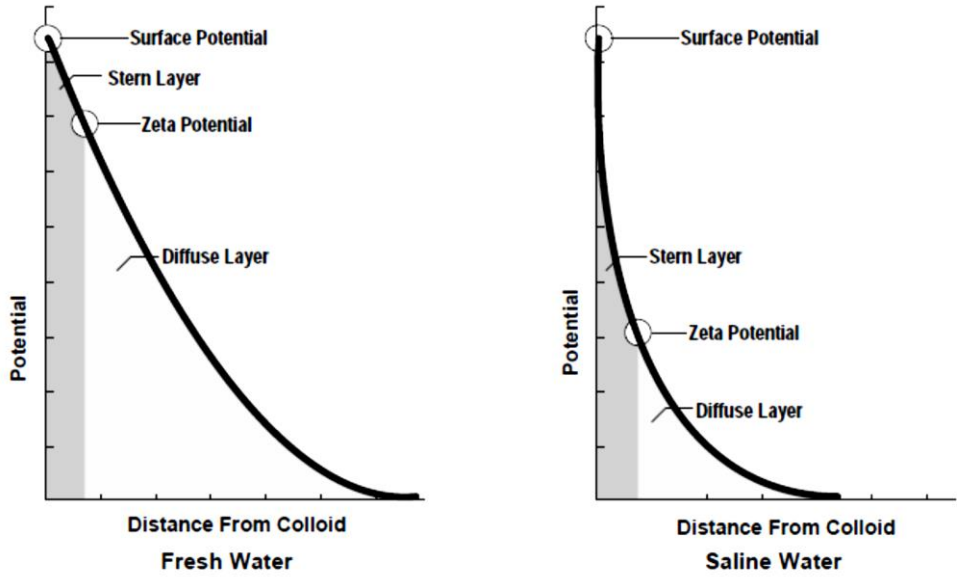

Figure 10.5. Changes in zeta potential, stern layer and DDL when comparing different water sources (Ravina & Moramarco 1993).

10.1.2.3.2 Zero Point Charge

A colloidal system will have zeta potential of zero at the point of zero charge (PZC). The PZC refers to the point the electrical charge density is equal to zero on the surface (Russel et al. 1992). At the PZC, there is minimum colloidal stability, maximum viscosity of the dispersion and maximum solubility of the solid phase. Another way to describe the PZC is that it is the pH value at which the a solid submerged in an electrolyte exhibits zero net electrical charge on the surface (Lyklema 2005; Russel et al. 1992). The surface participates in cation attraction and the cation exchange reactions when the surface has an anionic charge, and the pH values are above PZC. However, if the PZC is higher than the pH, then the surface will attract anions and take part in anion exchange reactions, with a positive net charge (Mahmood et al. 2011).

Many different methods have been proposed to determine the point of PZC in soils. Usually when studying soils, potentiometric titration is used (Appel et al. 2003). This method determines the point of zero salt effect (PZSE) by using the changes in the activity of H^+ and OH^- to assess the changes in surface potential. The other commonly used method to assess the point of zero net charge (PZNC) is non-specific ion adsorption (Mahmood et al. 2011). This method correlates the activity of H^+ and OH^- with the changes in the electrostatic adsorption of a cation and anion.

10.1.3 Soil pH and alkalinity

10.1.3.1 *Influence of soil pH*

Soils of dry regions, like a significant landscape of Australia, are usually ones with an alkaline pH and a strong presence of Ca, Mg, Na, and K as exchangeable cations. Since these are the base-forming cations, hydrolysis of these cations tends to cause an alkaline pH of soils (Brady & Weil 2002). There is no dispersion if a soil has a pH equating to the point of zero charge. If a soil has a net negative charge, then development of a diffuse double layer is expected and dispersion expected beyond -30 mV zeta potential. Clay particle flocculation often occurs at very low and very high pH values (Haynes & Naidu 1998), indicating pH values as important to the control of soil stability (Chorom et al., 1994).

Chorom et al. (1994) found that soil pH can be correlated with the dispersive potential of soils. In pure clay minerals, clay dispersion can be strongly affected by variations in pH (Chorom et al. 1994; Suarez et al. 1984). The amount of variable charge on the external surface of the clay particles decides the effect of pH on the electrical potential of clay surfaces. Chorom et al. (1994) showed that the pH changes the net charge present on clay particles and therefore, affects the clay dispersion. This makes net negative charge a primary factor in clay dispersion (Table 10.4).

Table 10.4. Dispersible clay as a % of total clay of Na-saturated soils from South Australia at different pH values (Source. Chorom et al. (1994))

Soil	pH values			
	4	6	8	9
Claremont (Smectite dominant) 4	16	40	48	
Evans (Illite dominant) 7	14	20	28	
Meadows (Kaolinite dominant) 2	6	10	12	

10.1.3.2 *Effect of alkalinity*

Alkaline soils (mostly clay soils) are soils with a high pH (> 9), poor soil structure and a low infiltration capacity (Hopkins et al. 2007). They are not saline, i.e. the total amount of soluble salts, especially sodium chlorides is not excessive (ECe < 4 to 8 dS/m). Often they have a hard calcareous layer at 0.5 to 1 m. depth (Abrol et al. 1988). Factors which make the soils alkaline include (i) poor drainage in arid region, (ii) rapid evaporation of alkaline soil solution, and (iii) excess uptake of alkaline salts and little percolation (Srivastava et al. 2002).

Alkalinity problems are more pronounced in clay soils than in loamy, silty or sandy soils due to their larger specific surface areas (Richards 1947). The clay soils containing montmorrillonitic or smectitic minerals (swelling clays) are more subject to alkalinity problems than illitic or kaolinitic clay soils (Srivastava et al. 2002).

10.1.4 Organic matter

Organic matter refers to material produced from the breakdown of plant and animal residues (Baldock & Nelson 2000). Humus is created when organic matter decays and the molecules of the humus cement particles together into aggregates which do not break down into water (Baldock & Nelson 2000). By increasing aggregation, an improvement in soil structure can be made and by increasing aeration, infiltration and percolation (Boyle et al. 1989). An increase in permeability also increases the soils' ability to take up water. According to Barzegar et al. (1997), the four elements that control clay dispersion are i) Soil characteristics, ii) level of sodicity, iii) the scale of mechanical disturbance and iv) the nature of organic matter. Organic matter can play the role of a binding and or dispersing agent. This role is dependent on many soil factors and interactions (Nelson & Oades 1998). For example, when covalently bonded organic molecules reduce the hydration charge, the amount of clay swelling and dispersion is reduced (Ezlit et al. 2010). Other factors influencing the role of organic matter include CEC, ESP and clay mineralogy (Marchuk et al. 2013a).

The bonding between the organic molecules determines the impact on the soil structure. Quirk (1994) states that organic matter, which can stabilise soil aggregates against slaking, can also induce clay dispersion. If bound by monovalent cation, it leads to the breaking of bonds and increasing dispersion. However, if bound by Ca-bridging, the dispersion can be reduced (Marchuk & Rengasamy 2010). Organic anions are known to increase clay dispersion by increasing the net negative charge of soil particles (Emerson & Smith 1970). When the organic matter contributes to the increase in hydration charge, swelling and dispersion are enhanced. Thus, the prevention of swelling and dispersion of soil aggregates by organic matter depends on the mechanisms involving reduction of net hydration charge (Oades 1984).