STRATEGIC USE OF ALKALINE IRRIGATION WATER: SOIL STRUCTURAL CONSTRAINTS AND PREDICTIVE AMENDMENT MANAGEMENT

A thesis submitted by

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Abstract

Land application of marginal quality irrigation water is a progressively increasing practice in many agronomic regions throughout the world, due to freshwater limitation and increasing demand for food and fibre. The use of marginal quality water can increase the potential for soil degradation and limit crop production in the long-term. Irrigation with such water that contains an excess amount of alkaline ions requires a strategic and appropriate management to avoid the potential detrimental impacts on the soil resource through considering the quality of water, soil type and site condition, and irrigation practice. This research project mainly focuses on enhancing the current understanding of practical strategies for utilising alkaline water as an irrigation water resource. This is achieved via assessment of the deleterious impact of alkaline irrigation water on soil physicochemical properties, investigation of the ability of models to simulate alkalinity condition, and land amendments with acidifying materials.

The effects of pH on the soil structural degradation were investigated in the laboratory using nine Australian soils with contrasting properties. The soils were leached with irrigation water of varying EC, SAR and pH (6, 7, 8 and 9). The outcomes of this study indicated that the increase of pH results in the increase of net negative charge on clay particles, consequentially causing greater: exchangeable cation at the clay surface, negative zeta potential, clay dispersion and movement of dislodged particles into pore spaces. Subsequently, saturated hydraulic conductivity (K_s) reduction occurred at a greater magnitude. Results reinforced that the effect of pH on the K_s is soil-specific depending on the original pH, clay content and clay mineralogy of soils.

The K_s reduction data were used to develop a generalised linear function, similar to the current function presented in HYDRUS model — developed from three American soils. A nonlinear (pedotransfer) function was also produced based on these nine local soils using the Levenberg–Marquardt optimisation algorithm, considering pH and electrical conductivity (EC) of the applied irrigation water, as well as the soil clay content. Comparison of the observed K_s reduction with the predicted outputs of these functions indicated that the models performed objectively well, successfully describing K_s reduction due to the pH. The nonlinear function improved the estimation

of the pH scaling factor for K_s reduction to operate as a function of soil specificity in the HYDRUS model, and needs to be considered in future HYDRUS model developments and use.

The functions developed for HYDRUS were developed under saturated hydraulic conditions in short columns, meaning that it was prudent to validate their performance for both unsaturated and longer soil columns using acidic, neutral and alkaline soils. The hydraulic conductivity data from the column experiments were used to validate the developed generalised and nonlinear functions as suitable for variably saturated conditions and superior to the existing HYDRUS function. Hydraulic conductivity prediction was greatest for the nonlinear (pedotransfer). The HYDRUS model was reasonably able to predict the change in EC and SAR, but unable to simulate pH and alkalinity appropriately. This suggests that the soil hydraulic conductivity reduction scaling factor function requires updating in HYDRUS to serve the majority of soils, preferably such that soil-specific nuances can be captured.

To strategically utilise alkaline water as an irrigation source, an investigation to improve current threshold electrolyte concentration (C_{TH}) semi-empirical equations via incorporation the alkaline anion (HCO_3^-) was undertaken. The current semi-empirical disaggregation model approach of Ezlit et al. (2013) is only based on the sodium and calcium system, without considering the adverse effects of alkalinity (i.e. HCO_3^-) to reduce K_s. The results indicated that an increase in HCO_3^- results in K_s reduction, even at low concentration (as low as 100 mg L^{-1}), and it is dependent on soil type. The results also demonstrated that there was a great association between K_s reduction for non-alkaline and alkaline irrigation water solution SAR and adjusted SAR (SAR_{adj}) for up to 30% K_s reduction. This suggested that HCO_3^- can be successfully incorporated into the current disaggregation model to determine C_{TH} (≤20% K_s reduction) to provide an indication of alkalinity effects on soils without having to conduct experimentation for C_{TH} beyond the current methodology of Ezlit et al. (2013).

Finally, the usefulness of marginal quality alkaline water was investigated within the field in order to demonstrate that there are suitable treatment options that can be land applied, and to investigate the capability of HYDRUS to model the expected outcomes. This study addressed the efficacy of gypsum and sulphur under irrigation with alkaline groundwater, on two Dermosol soils in New South Wales, Australia. The results indicated that the addition of sulphur source is an efficient strategy to address the alkalinity of irrigation water. The application of gypsum and sulphur performed well to reduce pH, alkalinity and SAR, and improved soil solution electrolyte concentration as well as increasing cotton yield. This supported the improvement in soil structure and permeability based on the predicted C_{TH} analysis for EC and SAR_{adj}. The predicted results demonstrated that the HYDRUS model suffers from some issues in predicting pH, HCO_3^-, EC and SAR within the soil profile overtime, but remains useful in helping design land amendment strategies provided model limitations are reported with presented strategies by practitioners.

This thesis research clearly highlighted the potential for strategic use of alkaline irrigation water, resulting in useful discussion identifying the limitation of guidelines and regulations. The work has highlighted the debility of the current C_{TH} determination and the HYDRUS model to predict soil structural degradation under alkalinity conditions, providing outcomes and pathways to improve both. This study culminates by providing a framework for the strategic use of alkaline water for irrigation, with suggestions for Australian guidelines to consider alkalinity under a general use approval (GUA) and beneficial use approval (BUA) system. The GUA and BUA system simultaneously provides irrigators freedom to operate and protects the environment as a general approach, as well as providing an application based system to irrigate on a soil specific basis where receiving environment and land amendment strategies can be demonstrated as suitable.

Certification of Thesis

This thesis is entirely the work of Aram Mohemed Ali except where otherwise acknowledged. The work is original and has not previously been submitted for any other award, except where acknowledged.

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Statement of Contribution

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Chapter 4.

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Abbreviations and acronyms

CEC	Cation exchange capacity
ESP	Exchangeable sodium percentage
EDP	Exchangeable dispersion percentage
ECR	Exchangeable cation ratio
SAR	Sodium adsorption ratio
SAR_{eff}	Effective SAR
SAR_{ADJ}	Adjusted SAR
CROSS	Cation ratio of soil structural stability
EC	Electrical conductivity
DDL	Diffuse double layer theory
EDL	Electrical double layer
StDev	Standard deviation
ICP-MS	Inductive coupled plasma atomic mass
K	Hydraulic conductivity
K_s	Saturated hydraulic conductivity
r_{Ks}	Relative saturated hydraulic conductivity
K_r	Relative saturated hydraulic conductivity
$K(h)$	Unsaturated Hydraulic conductivity
K_{red}	Hydraulic conductivity
CSG	Coal seam gas
OC	Organic carbon
DOC	Dissolved organic carbon
XRD	X-Ray diffraction
CFC	Critical flocculation concentration
PCO_2	Carbon dioxide partial pressure
RSC	Residual sodium carbonate
ζ-potential	Zeta potential (-mV)
HSD	Tukey’s honest significant difference
C_{TH}	Threshold electrolyte concentration
C_{THadj}	Adjusted threshold electrolyte concentration for alkalinity
ANOVA	Analysis of variance
ANZECC	Australian and New Zealand Environment and Conservation Council
r	K_s reduction scaling factor
r_1	K_s reduction scaling factor for EC&SAR
r_2	K_s reduction scaling factor for pH
r_{SF}	Relative scaling factor
r_{LM}	Scaling factor determined using the Levenberg-Marquardt optimisation algorithm for pH, EC &SAR
CC	Percentage of clay content
RMSE	Root mean square error
ALK	Alkalinity
QLD	Queensland state
NSW	New South Wales state
USDA	United States Department of Agriculture
θ_r	Residual water content
θ_s	Saturated water content
$\theta(h)$	Volumetric water content
C_o	Total salt concentration
ρ	Bulk density (g cm^{-3})
n	Pore size distribution
l	Tortuosity pore connectivity parameter
PZC	point of zero charge
pHZPC	pH of zero point charge
IA	Index of agreement
MAPE	Mean absolute percentage error
ET_o	Evapotranspiration
ET_c	Crop evapotranspiration
RCBD	Randomized complete block design
FC	Field capacity water content
GPS	Global positioning system
GIS	Geographical information system
NTU	Nephelometric Turbidity Units
AU$	Australian dollar

1. Introduction and Aims

1.1. Background

Worldwide, there is an increasing demand for food and fibre due to the rapid growth of the world’s population which is predicted to reach 9.1 billion by 2050, resulting in relative increasing food demand from 58% to 98% (Nature editorial, 2010; Valin et al., 2014). The need for food supply requires efficient and sustainable agricultural land management because 95% of the world’s food supply comes from agricultural land, while less than 1% is from oceans and other sources (Pimentel et al., 1994). Water is considered the most important resource for irrigation along with soil, for sustainable agriculture. Currently, there is immense pressure placed on fresh-water resources, due to climate change (prolonged drought) and the increasing demand for agricultural and other uses (e.g. in the industrial sector). This results in growing demand and competing priorities for freshwater resources, leading irrigators to look for alternative water sources. As a result, greater importance is being placed on the strategic use of low-quality water as a resource (Hall et al., 2008). The irrigation sector uses about 70% of the freshwater withdrawal worldwide (Renner, 2012). Strategic use of low-quality groundwater and industrial water resources is now globally more important in order to sustain agriculture in water-limited environments and to augment the fresh-water reserves (Ezlit et al., 2013; Raine et al., 2007; Sharma & Minhas, 2005). Marginal quality water is defined as that which poses a risk to sustainable agriculture by virtue of its quality, though it can be safely used for irrigation with precautionary management (Abbott & Hasnip, 1997; Ezlit et al., 2010; Qadir et al., 2007b). In the context of this study, the term “marginal quality water” refers to alkaline water and associated sodicity and salinity that poses a risk to the agricultural soil system.

The rapid increase of the coal seam gas (CSG) industry throughout Australia has also increased interest in the use of groundwater that is alkaline, sodic and saline, and produced as a CSG by-product for irrigation purposes (Bennett et al., 2016b; McKenna et al., 2019; Raine & Ezlit, 2007). The use of marginal quality irrigation water increases the risk of deteriorating soil function (Cook et al., 1994; Shainberg & Letey, 1984), with consequent damage to crop production (Rengasamy,

2010) where the use of poor quality water has not been well guided or appropriate ameliorative actions taken. The use of poor quality groundwater and industrial wastewater (with high pH, sodicity and salinity), may have an adverse influence on the structure and permeability of soils, due to the development of sodicity and accumulation of alkaline salts (Halliwell et al., 2001; Rengasamy, 2006; Szabolcs, 1989). It is on this basis that the water quality must be considered and planned for prior to land application. The quality of groundwater is often variable within a given region and is associated with the lithology of geological formations that yield the water—for example, containing bicarbonate, sodium, calcium and other chemical ions (Cartwright et al., 2012; Kinnon et al., 2010). This means that planning for the use of these waters must also be variable, with further consideration also provided to soil variability.

Alkalinity is of concern as it affects one-third of the world's soils (Guerinot, 2007), and approximately a quarter of Australian soils (Northcote & Skene, 1972). The latter are largely situated in current crop production regions. A large proportion of these agricultural lands are sodic and alkaline, with the occurrence of this for more than 80% of irrigated soils being closely linked directly with irrigation management and irrigation water quality (Rengasamy & Olsson, 1993). Alkalinity, along with salinity and sodicity, is considered as a soil constraint, and alkalinity is categorised as a part of saline soil problems, developed from the application of alkaline irrigation water resources and dryland conditions (Gupta et al., 1984; Rengasamy, 2010). The major contributing ions to alkalinity are bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). It follows that alkalinity develops a buffering capacity within the soil solution and causes an increase in the solution pH. This further results in the increase of sodium in ratio to other solution cations, whereby Ca is removed in the formation of relatively insoluble precipitates within the root zone (Hillel, 2013). Build-up of sodium within the root zone frequently occurs due to the improvement of water use efficiency resulting in insufficient leaching fraction (Shaw & Thorburn, 1985) to move salts and alkaline anions below the root zone in arid and semi-arid zones (Raine et al., 2007), and where appropriate steps to treat the soil percolate were not taken prior to application (Bennett et al., 2016b; McKenna et al., 2019). Symptoms associated with alkalinity are poor soil structural stability, smaller pore size, low water infiltration, plant growth, and imbalance of nutrients in the soil (Kuehny & Morales, 1998; Rengasamy, 2002b), although these are not ubiquitous to alkalinity effect of soil structure (i.e., the effects of sodicity and compaction) meaning that alkalinity is often overlooked in the practical application of irrigation systems.

Where the sodium adsorption ratio (SAR) is considered to be appropriate for irrigation of a given soil (ANZECC, 2000; Bennett et al., 2019a; US Salinity Laboratory Staff, 1954), ignoring the solution alkalinity (i.e., high pH) can exacerbate the influence of sodium within the soil system resulting in what was thought to be appropriate water actually being inappropriate for use without further treatment. High sodium is often associated with a high level of dissolved carbonate and, concomitantly, high pH (Suarez et al., 1984), due to the existence of precipitated calcium carbonates and sodium carbonates. As a result, the sodium becomes a dominant ion in the soil solution, causing soil structure degradation and plant growth restriction due to poor soil, water and air relations (Rengasamy & Olsson, 1991). Suarez et al. (1984) and Marchuk (2013) stated that the effects of alkalinity and exchangeable sodium percentage (ESP) on physicochemical properties and crop growth are not easy to be distinguished, because high pH and high ESP often occur together; it is important to note that neutral and acidic soils can also be sodic. In terms of soil structural stability under alkaline conditions, previous studies confirmed that soils behave differently, resulting in elevating the exchangeable sodium percentage (ESP) level and alkalinity build-up, subsequently increasing clay swelling and dispersion and lowering permeability (Ben-Hur et al., 2009; Cucci et al., 2015; Ghiberto et al., 2007; Gupta & Abrol, 1990).

To assess the suitability of water for irrigation, the threshold electrolyte concentration (C_{TH}) has been proposed as the appropriate limit to determine the soil-specific reduction in saturated hydraulic conductivity (K_s) as a function of solution salinity (EC) and sodicity (SAR). The C_{TH} is documented as a reduction in K_s of between 10–25%, defining a measurable departure from a potential minima (Ca saturated system) within the error of the measurement method (Bennett & Raine, 2012b; Ezlit et al., 2013; McNeal & Coleman, 1966; Quirk & Schofield, 1955; Shainberg et al., 1981). These studies state that the K_s reduction due to exchangeable sodium percentage (ESP) and electrolyte concentration (EC) is associated with clay swelling, disaggregation and dispersion, and is highly soil specific (Bennett et al., 2019a; Bennett & Raine, 2012b; Shainberg & Letey, 1984; Shainberg & Singer, 1990). The C_{TH} can be used as a criterion for the appropriate selection of saline-sodic water to maintain soil permeability, although this is laborious and the current methodologies are based purely on a Na:Ca system. Dang et al. (2018c) have demonstrated that there are difficulties in the incorporation of K into the C_{TH}, but propose that the results in their approach could be used as a conservative measure for the effect of K on soil structure in equivalence to a Na effect (see: Zhu et al. (2019b)). Additionally, Zhu et al. (2019a) show that Mg does not result in dispersion, but confirm the differential behaviour of Mg to Ca and that this too is not directly equivalent to a generalised critical flocculation coefficient, but rather a soil-specific one (see: Zhu et al. (2019b)). On this basis, quantitative prediction for the effect of solution cation suite on soil structure has not yet been fully established. Similarly, the effect of alkalinity within the C_{TH} criterion has not been demonstrated. The question remains as to whether or not SAR equations modified for the inclusion of alkalinity (i.e., Equation 1.1 and Equation 1.2) would allow direct incorporation of alkalinity into the disaggregation model of Ezlit et al. (2013).

$$SAR = \frac{[Na]}{\sqrt{0.5([Ca] + [Mg])}}$$

Equation 1.1

$$SAR_{adj} = \frac{[Na]}{\sqrt{0.5([Ca_{eq}] + [Mg])}}$$

Equation 1.2

where all ion concentrations are expressed in $\text{mmol}_c\ L^{-1}$. The unit of measure is $(\text{mmol}_c\ L^{-1})^{0.5}$ for SAR and SAR_{adj}. Ca_{eq} represents the expected Ca concentration after equilibrating with the bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) during solution application.

In recent decades, mathematical modelling has become an alternative tool to analyse and manage water and soil solution movement and accumulation of salts. The HYDRUS-1D (Šimůnek et al., 1998) software package, as a finite model, numerically solves the Richards (1931) equation for one dimensional saturated and unsaturated water movement and an advection-dispersion equation for heat and solute transport. This model utilises the basis of the C_{TH} phenomena in its hydraulic reduction rationalisation through the McNeal (1968) model, although should be updated with the Ezlit et al. (2013) model that supersedes this. Additionally, HYDRUS-1D includes the effects of solution pH associated with soil structural degradation as a basic hydraulic reduction coefficient based on a limited sample of three soils from America (Suarez et al., 1984). This approach treats the effect of solution alkalinity and pH as independent to the SAR and EC effect on soil structure, which is not necessarily sensible. The HYDRUS hydraulic reduction function can be expressed as:

$$K_{red}(pH) = \begin{cases} 1.0, & \text{for } pH < 6.83 \\ 3.46 - 0.36pH, & \text{for } 6.83 < pH < 9.3 \\ 0.1, & \text{for } pH > 9.3 \end{cases}$$ **Equation 1.3**

In the case of Equation 1.3, it can be seen that the pH based reduction coefficient may be provided more weight than it should be allowed in treating it as an independent term. Furthermore, the reduction in soil hydraulic conductivity (K_{red}) is highly soil-specific where marginal quality irrigation water is applied (Bennett et al., 2019a). The ability to incorporate this complexity does not exist in the current HYDRUS reduction equations. Solution chemistry kinetic reactions and exchange flow modelling can be determined by using the PHREEQC (Parkhurst & Appelo, 1999) model, although soils are an inherently heterogeneous and complex material (Miller & White, 1998), meaning, the interaction of predictable solution kinetic reactions becomes a much more complex task when considering exchange processes in similar soils with vastly different C_{TH}. Unless the specificity of the C_{TH} can be built into the geochemical reactions predicted in PHREEQC, which is unlikely at this point, there is greater merit in seeking to move towards understanding the level of control ascribed to the HYDRUS pH based hydraulic reduction coefficient and seeking to improve this. Therefore, the current mathematical models require evaluation and validation for soils with unique C_{TH}, in order to be used to predict the effects of solutes, their reactions, change in the soil dynamic pore relations, and related management options.

In Australia, the irrigation water guidelines (ANZECC, 2000) present no trigger value for alkalinity concerning the suitability of irrigation water to maintain soil structure and permeability. In general, it is reported that alkalinity greater than 100 mg L^{-1} can affect plant growth, irrigation equipment and soil properties (ANZECC, 2000; DAF, 2014), but this is not used as a value to suggest to the practitioner that the water should not be used for irrigation on the basis of soil structural issues discussed above. At the very least, the ANZECC guidelines should provide guidance around appropriate and strategic soil and water alkalinity management as important factors to minimise the negative effects of alkalinity on physicochemical properties and plant growth.

The reclamation of alkaline soil and irrigation water is possible and requires dissolution of accumulated calcites through using acid-forming materials and supplying a source of calcium (Ca^{2+}) that can replace the excess exchangeable sodium within the soil system (added directly to the soil and/or within irrigation water) (Ali et al., 2018; Bennett et al., 2016b; Johnston et al., 2013; McKenna et al., 2019). Calcium as a divalent ion, in the correct concentration, will maintain the soil in an aggregated condition, negating soil dispersion and minimising disaggregation (Dang et al., 2018a; Zhu et al., 2019a). It is well understood that alkalinity issues can be resolved by neutralising the pH of soils and irrigation water (Figure 1.1).

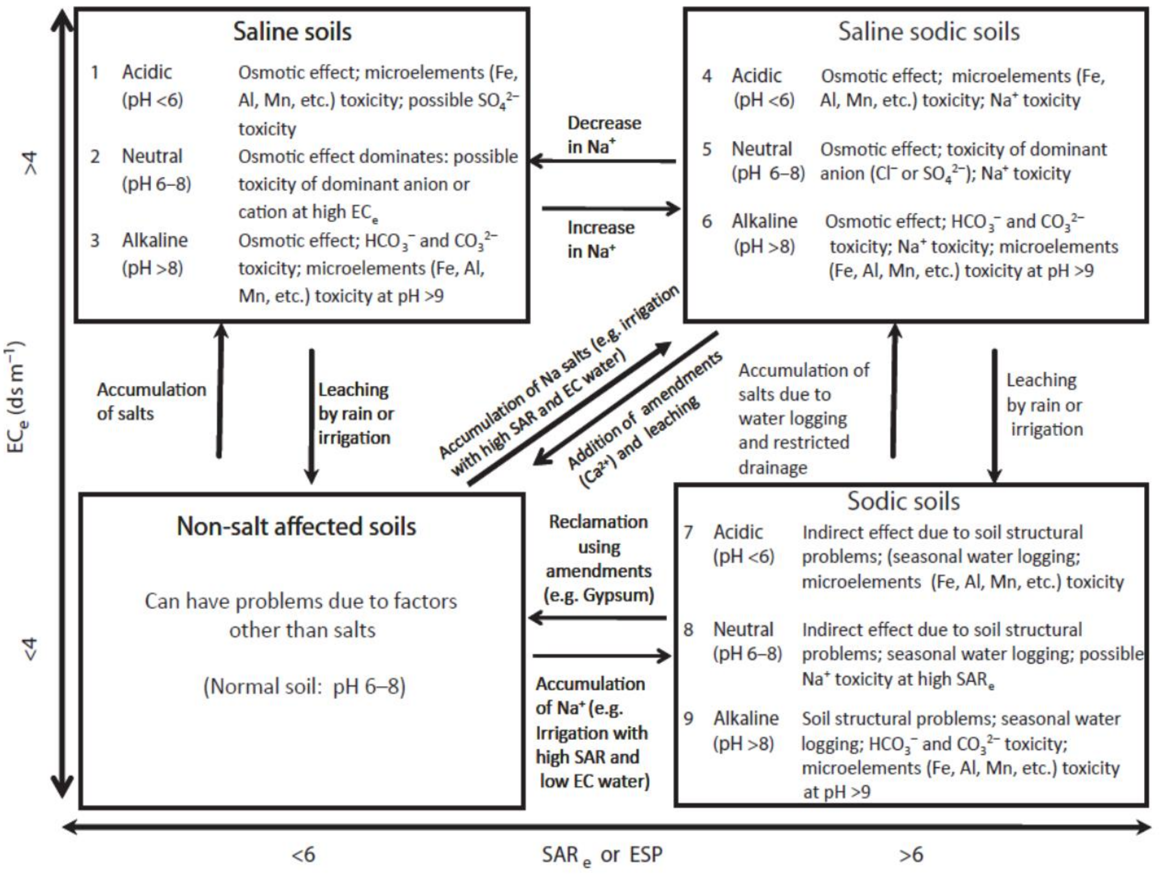

Figure 1.1 Categories of salt-affected soils based on ECe (dS m^{-1}), SAR_e, and pH 1:5 of soil solutions (Rengasamy, 2010). EC_e and SAR_e are extracted electrical conductivity and calculated SAR from cations in extracted soil solution.

Amendment materials such as gypsum ($CaSO_4$. $2H_2O$), sulphur (S) and sulphuric acid (H_2SO_4) have been widely utilised for lowering pH and supplying Ca^{2+}. While these amendment materials have the potential to lower pH, avoid calcium precipitation, improve soil aggregate stability, and maintain/increase K_s of soils (Chorom & Rengasamy, 1997; Mace et al., 1999), they are not frequently utilised within the agricultural sector. A further body of evidence for the efficacy of these materials within the agricultural context to simultaneously address irrigation solution alkalinity and sodicity would be beneficial, and potentially work towards a framework for soil-specific amendment requirements with cost-benefit from this consideration.

The current focus on marginal quality water has mainly been on the sodicity and salinity aspects of water quality, with less, if any, concern placed upon alkalinity. Incorporation of the alkalinity effect with sodicity and salinity is prudent so as to allow land managers reliable means to manage their lands without undue environmental harm. Moreover, there is a lack of appropriate guidelines in utilising alkaline irrigation water strategically to maintain soil health and sustain agricultural production. Application of alkaline water on a strategic basis is possible if appropriate models are developed to predict the change in soil stability and hydraulic dynamics incorporation with salinity and sodicity based on the soil specific effect. Assessment of field conditions, laboratory and mathematical models will be required in evaluating the efficacy of any framework for management advice. The development of enhanced practices and identification of soil behaviour under different levels of alkalinity will help to reduce uncertainty in predicting the change in soil properties and promote considerable adoption of sustainable land-use practices. Such assessment schemes would be beneficial in the evaluation of soil stability, in minimising the inherent risks associated with marginal quality waters and enhancing the sustainability of irrigation industries. This is particularly important for Australia, due to the current and progressing increase of CSG water development, expanding agricultural sector interest in marginal and industrial waters, as well as informing regulations for environmental protection within specific regions.

1.2. Rationale of this study

The strategic use of marginal quality irrigation water for agricultural production is important in water-limited environments and with increasing demand for food and fibre. Thus, there is also increasing demand placed on the soil and water resources to increase production in the agriculture sector. Information pertaining to the effects of alkalinity on soil physicochemical properties is not as well documented as it could be and is limited in terms of considering soil variation and soil-specific effects, especially for Australian soils. Therefore, this study is established to bridge the gap between potential strategies and sustainable practices for the use of alkaline irrigation water as a strategic agricultural resource, and through amending alkaline Australian soils. Moreover, the study seeks to formulate a framework to predict and contribute to practical management. This must be based on soil and water analysis used to parameterise thermodynamic models for Australian soils based on their clay mineralogy, and physicochemical characteristics when subject to alkaline waters. Therefore, this study is designed to improve the modelling of water and solute movement, as well as use these to better define appropriate management strategies to improve soil structural stability. Elimination of salinity, sodicity and alkalinity soil constraints linked with irrigation management would result in approximately AU$1,122 million per annum in additional benefits for the Australian economy (Hajkowicz & Young, 2005; Rengasamy & Olsson, 1993). Thus, this research focuses on the practical management of irrigation water alkalinity leading to avoidance and/or management of such soil constraints. Alkalinity is inherent to many Australian soils and irrigation waters, meaning that they are potentially underutilised. This project will help to determine the extent of this potential, developing management approaches considering poor to marginal water qualities, and soil-borne treatment of this, with the view to lessening negative effects on the environment, benefiting the Australian economy, and increasing agricultural productivity.

1.3. Specific objectives of the research

The principal aim of this study is to enhance the current understanding of adverse effects of alkaline irrigation water on Australian soils, with a focus on the modelling of water and solute movement by taking into account the change of soil hydraulic properties under alkaline conditions. Also, this thesis addresses the development of strategic practices and understanding about the effects of alkaline water on soil structural stability, as well as appropriate management in the agricultural sector. Therefore, the main objectives of this research are to:

- Determine the extent of soil structural degradation associated with the application of alkalinity and high pH in irrigation water on a range of different soils.

- Evaluate the applicability of the soil hydraulic reduction factor in the HYDRUS-1D model associated with the alkalinity of Australian soils. Subsequently, if it is found to be lacking, develop a new approach, or update the existing model.
- Assess the ability of the current HYDRUS-1D model to predict hydraulic property changes and solute transport parameters within a shallow soil profile, associated with major rooting depths of cereal crops, under alkaline irrigation water application.
- Determine the extent of the adverse effects of alkaline irrigation water on soil hydraulic conductivity reduction prediction with variable levels of sodicity and salinity in determining the threshold electrolyte concentration for incorporation into the model of Ezlit et al. (2013).
- Assess the potential management strategies to ameliorate alkaline soils and water to increase soil hydraulic conductivity, maintain soil structural stability and productivity within a field based agricultural context.

1.4. Thesis overview

Chapter 1: Introduction and Aims

This chapter introduces the broad issues associated with soil alkalinity and provides initial background concerning alkaline irrigation water and alkaline soils. It identifies various concerns about the strategies for use of alkaline irrigation water, management of alkalinity and introduces the aims of the study in relation to these. It sets out the scope of the work, identifies the aims and objectives and provides an overview of the ensuing chapters.

Chapter 2: Literature review

This chapter presents the detailed background information associated with the current research, highlighting the knowledge gaps that further support the justification for this study. This chapter covers: i) the conceptual framework of soil constraints caused by irrigation water alkalinity and the issues associated with alkalinity on soil physicochemical properties and plant growth; ii) the mechanisms of alkalinity and pH, and the relative importance of the various processes controlling these effects on soil degradation; iii) the management implications for the use of alkaline irrigation water and identification of soil amendment and irrigation water treatment strategies; and iv) a review of current soil-water and solute modelling.

Chapter 3: General methodology

This chapter introduces the soils used for this research and the major attributes of each soil. This includes the geographical location of each site, current condition, the climate, mean annual rainfall, chemical composition, physical properties, and clay mineral suite. A detailed description of the common methods used in this study is also presented and the specific methodological details for each experiment are described in the relevant chapters. The methodologies applied herein are most appropriate considering the study's objectives.

Chapter 4: Effect of irrigation water pH on saturated hydraulic conductivity and electrokinetic properties of acidic, neutral and alkaline soils

Chapter Four investigates and discusses the impact of irrigation water pH on the saturated hydraulic conductivity, cation exchange capacity, net particle charge and dispersivity of soils. Nine soils with differing pH, alkalinity, clay content and mineralogy were examined in leaching column experiments with solutions of varying pH, sodium adsorption ratio and electrical conductivity. The results are presented and discussed on a laboratory basis.

Chapter 5: A pH based pedotransfer function for scaling saturated hydraulic conductivity reduction: Improved estimation of hydraulic dynamics in HYDRUS

This chapter reviews and evaluates the pH scaling factor for saturated hydraulic conductivity reduction in the HYDRUS model. The limitation of the current pH scaling factor is described and new generalised function and nonlinear pedotransfer functions are also developed using hydraulic conductivity reduction data obtained from the laboratory study (Chapter 4). The current pH scaling factor in the HYDRUS model and a newly developed function were evaluated and validated, providing suggestions to enhance the HYDRUS model prediction.

Chapter 6: Assessing the hydraulic reduction performance of HYDRUS-1D for application of alkaline irrigation in variably-saturated soils: Validation of pH driven hydraulic reduction scaling factors.

Chapter Six presents an evaluation of the ability of the HYDRUS-1D model to predict the changes in chemical properties and hydraulic dynamics of an acidic, a neutral and an alkaline soil subjected to alkaline irrigation water application. The simulation data were compared with data obtained from the laboratory study using columns under unsaturated soil-water conditions. The developed generalised and nonlinear functions were compared to the current HYDRUS model and validated based on the observed hydraulic conductivity dataset.

Chapter 7: Incorporating solution alkalinity into a hydraulic reduction model to account for disaggregation and dispersion

This chapter focuses on the incorporation of alkalinity (HCO_3^-) into the semi-empirical disaggregation model approach to determine threshold electrolyte concentration (C_{TH}). The significance of alkalinity incorporation into disaggregation is described and limitations for the incorporation are demonstrated and discussed.

Chapter 8: Planning land management strategies for application of alkaline and sodic groundwater on two soils in New South Wales

Chapter Eight investigates and discusses the efficacy of application of gypsum and sulphur alone and their combination with lime to neutralise the alkalinity and sodicity of applied groundwater in two alkaline Dermosol soils in New South Wales, Australia. The HYDRUS-1D model was also used to predict the dynamic changes in soil solution under land amendment and alkaline irrigation water. The changes in soil properties are presented for different periods (up to two years and no less than three months) after initial amelioration application. The viability of using amendments is analysed and discussed using data collected on pH, electrical conductivity, alkalinity and soluble cations for soil solutions as well as cotton yield data. The electrolyte effects and sodium adsorption ratio data are used to estimate the improvement in soil aggregate stability based on the determined threshold electrolyte concentration for each soil.

Chapter 9: General discussion, conclusion and future research directions

The concluding chapter discusses some of the implications of the key findings of the various experiments and discusses these analytically in terms of the principal aims of the study. It presents a framework for approaching the assessment of alkaline irrigation water for strategic irrigation, the provision of treatment recommendations, as well as the considerations for on-farm feasibility. It also emphasises the outcomes that serve the strategic use of alkaline irrigation water and its potential to reform Australian irrigation water guidelines and management practices for alkaline irrigation water. The general conclusions are subsequently presented and recommendations for future research as a result of this study are detailed.

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2. Literature review

2.1. Introduction

This chapter explores the conceptual framework of soil constraints caused by irrigation water alkalinity, with further consideration of sodic and saline soil systems interacting with this water quality. The review addresses the issues associated with alkalinity, focusing on the importance of irrigation water quality effects on soil physicochemical properties and plant growth. In addition, the mechanisms of alkalinity and pH, and the relative importance of the various processes controlling these effects are discussed. The reasons for soil degradation via alkaline, saline and sodic marginal quality irrigation water are detailed. Subsequently, the management implications for the use of alkaline irrigation water are covered and soil amendment and irrigation water treatment strategies are explored. Current soil-water and solute modelling are reviewed along with the models most widely used to quantify the alkalinity and pH effect on soil hydraulic dynamics. The review concludes with a summary of research suggestions required to be undertaken to enhance the current understanding of the application of alkaline irrigation water.

2.2. Soil and irrigation water alkalinity

2.2.1. Soil alkalinity

Alkaline soil refers to soils with a pH of 8.0 or higher (de Caritat et al., 2011). Alkalinity can be defined as a quantitative capacity of solutions to neutralise an acid due to the high concentration of hydroxides. Soil alkalinity is produced due to natural and anthropogenic causes (Brady & Weil, 2008). The natural development of alkalinity is due to the weathering of parent materials containing carbonates such as calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), the weathering of primary and secondary minerals, and the weathering of other carbonate materials in arid and semi-arid environments (Brady & Weil, 2008; Chapin III et al., 2011; Mattson, 2014; Merry, 2009). Soil alkalinity can also develop as a result of the application of marginal quality irrigation water (surface and groundwater), or floods containing a high amount of carbonate ions. Additionally, soil alkalinity may be associated with over-liming of acidic soils (Patel & Saraf, 2014). The alkalinity of soils varies both spatially (in the x, y and z dimentions) and temporally, due to differences in native soil forming process such as parent material, climate, and landscape characteristics, as well as land management strategies (Gregory & Nortcliff, 2012).

2.2.2. Water alkalinity

The alkalinity of natural water is developed when water passes through the soil profile and bedrock containing carbonate, bicarbonate and hydroxide compounds. For example, the majority of the water in the Great Artesian Basin in Australia has high sodicity and alkalinity, and high enough salinity (Biggs et al., 2010), that it is generally not suitable for direct application to soils (Ezlit et al., 2010). Water generally becomes highly alkaline when flowing through limestone bedrocks that are rich in carbonates, subsequently developing a large solution buffering capacity (Carlsen et al., 2004). Alkalinity inputs also occur due to the carbonate and bicarbonate compounds from food residues and industrial cleaning agents (Gomes et al., 2016). The use of such alkaline water for irrigation purposes without treatment leads to increased alkalinity in the soil system, resulting in soil constraints in soil and can have deleterious effects on soil physicochemical properties and plant growth (Gupta et al., 1984; Rengasamy, 2010). However, the extent to which such an effect occurs is site specific and depends also on the natural conditions of the soil, or the source of the industrial wastewater.

2.2.3. Sources of alkalinity

The major sources of carbonate come from soluble alkaline earth carbonates such as calcite, dolomite and other sources of carbonates. Calcite ($CaCO_3$) is normally the dominant form in most developed soils when occurring in its initial pedogenic origins (Nelson, 1982). Reddy and Wang (1980) stated that the native $CaCO_3$ is more soluble and has higher ionic activity in soil solution than pure calcite in a static state. Carbonate salts have different level of solubility in water (Windholz et al., 1976) (Table 2.1). Calcite, dolomite and other forms of carbonic pedogenic compounds have the potential ability to react with protons (H^+) to produce bicarbonates as well as releasing cations (Balistrieri et al., 1999; Sherman & Barak, 2000; Stumm, 1992).

$$\text{(Calcite)} \quad CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3{}^-$$

$$\text{(Dolomite)} \quad CaMg(CO_3)_2 + 2H^+ \leftrightarrow Ca^{2+} + Mg^{2+} + 2HCO_3{}^-$$

$$\text{(Ankerite)} \quad Ca(Fe_{0.61}, Mg_{0.24}, Mn_{0.093})(CO_3)_2 + 2H^+ \leftrightarrow Ca^{2+} + 061Fe^{2+} + 0.24Mg^{2+} + 0.093Mn^{2+} + 2HCO_3{}^-$$

Equation 2.1

At pH values above 7.0, the (H^+) concentration in the soil is low, which significantly promotes alkalinity formation. Additionally, the proton and base system is completely balanced, meaning that as the (H^+) concentration decreases, it is directly balanced in calculating the total alkalinity. Hence, the complete equation for alkalinity in soil with the contribution of HCO_3^-, CO_3^{2-}, and OH^- can be developed as described in Equation 2.2 (Manahan, 2010).

$$Alkalinity = [HCO_3{}^-] + 2[CO_3{}^{2-}] + [OH^-] - [H^+]$$

Equation 2.2

Table 2.1 Mineral solubility in water (Windholz et al., 1976).

Mineral	**Solubility (mol L^{-1})**
$CaCO_3$	0.00014
$MgCO_3$	0.002
Na_2CO_3	1.1

2.2.4. Residual alkalinity

An alternative index to measure the alkalinity hazard for soil is Residual Sodium Carbonate (RSC), which is used to assess the suitability of irrigation water, as well as to measure the Na^+ content in relation to Ca^{2+} and Mg^{2+} concentrations, to assess HCO_3^- and CO_3^{2-} hazards. High RSC could increase the pH and sodicity of the soil solution (Joshi et al., 2009; Prasad et al., 2001). The RSC is usually calculated via Equation 2.3 developed by (Eaton, 1950):

$$RSC = (HCO_3{}^{1-} + CO_3{}^{2-}) - (Ca^{2+} + Mg^{2+})$$

Equation 2.3

where all ion concentrations are expressed in $mmol_c\ L^{-1}$.

The classification of irrigation water according to the RSC values is illustrated in Table 2.1. In general, irrigation water with less than 1.2 mmol$_c$ L^{-1} is expected to be moderate or safe, and the hazard increases with increasing RSC. Very high RSC is considered unsuitable for irrigation unless it is treated with gypsum (Joshi et al., 2009; Nishanthiny et al., 2010). Lal et al. (1980) conducted a pot experiment using irrigation waters with RSC up to 9.5 mmol$_c$ L^{-1}. The authors demonstrated that with increasing RSC, the pH and exchangeable sodium percentage (ESP) of soil increased significantly, while infiltration rate decreased. Similarly, Ghiberto et al. (2007) found that RSC at values greater than 1.25 mmol$_c$ L^{-1} resulted in 10% and 79% reduced hydraulic conductivity, and increased ESP from 1 to 10%, for the topsoil and subsoil of a Mollisol soil, respectively.

Table 2.2 Irrigation water alkalinity classification, adapted from DAF (2010) and Rengasamy et al. (2010).

Alkalinity (mmol$_c$ L^{-1})	*Suitability for irrigation*
0–1.25	The impact of SAR is moderate
1.25–2.5	Increasing problems; use gypsum; not sodium sensitive crops.
2.5–5.0	High alkalinity
>5.0	Very high alkalinity; not suitable

2.2.5. Buffering capacity of soil and irrigation water

Buffering capacity is defined as the ability of soil solutions to maintain a given pH level when subjected to acid or alkaline agents (Aitken et al., 1990; Nelson & Su, 2010). Soil and water develop into a buffered system when containing a significant quantity of carbonate, since they can accept H^+, having the ability to resist change. Hence, the HCO_3^{1-} and CO_3^{2-} in soil and water provides resistance to rapid change in pH creating major buffering systems that control pH changes (Gupta et al., 1984; Kuehny & Morales, 1998; Lindsay, 1979). High buffering capacity can be achieved in the soil solution via the accumulation of alkalinity induced salts from the long-term of irrigation with high alkalinity water (Aguilar & Alonso, 2005). Additionally, acid application will not decrease soil pH linearly in high carbonate soils, due to the reaction of added H^+ with soil carbonates (Aitken et al., 1990).

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$$

Equation 2.4

$$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^- + CO_3^{2-} + H^+ \leftrightarrow HCO_3^-$$

The ability to determine or predict pH buffering capacity is beneficial for modelling pH-dependent processes within the soil and important in making practical decisions for the lime requirement of acid soils and acid required to neutralise alkaline soils. Buffering capacity can vary greatly depending on soil texture, mineralogy and organic matter content (Aitken et al., 1990) and the extent of sesquioxides (aluminum and iron coatings) on clay particle surfaces (Thomas & Hargrove, 1984). Therefore, to determine the buffering capacity of the soil, it is important to understand the physical and chemical properties of soil alkalinity, as carbonates act in developing and retaining a high pH value via their contribution in alkaline conditions and engagement to clay particles. The acid buffering capacity of soil has consequently been researched precisely and well documented in the literature, especially in Sposito (2008) and Nelson and Su (2010). Quantifying the alkaline buffering capacity of soils, and the correlation of this with the amount/ suite of carbonates and physical and chemical properties, will be valuable for productivity management of naturally occurring alkaline soils, and soils where alkaline waters are to be applied.

2.3. The effects of alkalinity on soil properties and crops

2.3.1. Relationship between alkalinity and pH

Most naturally formed soils have a pH ranging from 4–9, with the soil pH for a specific soil determined by the soil clay minerals, organic portion, associated ion exchange, and hydrolysis reactions (Sumner et al., 1991). That is, these factors determine the buffering capacity and the subsequent extent of reaction to a percolating solution of particular acidity/alkalinity. Mashhady and Rowell (1978) indicated that the main factors responsible for alkaline pH are the partial CO_2 pressure, concentration of CO_3^-, and HCO_3^- ions. In Australia, alkaline soils include Vertosols, subsoils of some Chromosols, and Sodosols and throughout Calcarosols.

As previously described, as the pH increases above 8.0, carbonates become dominant ions in the soil solution. Precipitation of calcium carbonates is a major process affecting soil solution chemistry and pedogenesis in arid regions (Bohn et al., 2015). The chemistry of carbonates at soil pH above 9.5 is different from situations when with the pH is between 8.2 and 9.5 (Rengasamy (2016) as the exchangeable Na^+ is generally increasing when soil pH increases (Abrol et al., 1980). Carbonic acid in soils start to decrease and increasing HCO_3^- with increased pH from 4.0 to 8.3, respectively, while carbonate anions increase at higher pHs (Lindsay, 1979) (Figure 2.1).

Figure 2.1 suggests that HCO_3^- is dominant above 6.3, but CO_3^{2-} is not dominant until above ~10.5. At 8.3 the presence of HCO_3^- is at its maximum and the others are essentially absent. Bicarbonate proportions decrease, but survive in soil solution, until approximately pH of 12 with increasing carbonate formation. It is important to note that, carbonate proportions increase at a rate 10 times faster than bicarbonates per unit increase in soil pH (Brady & Weil, 2008; Lindsay, 1979). Figure 2.2 demonstrates a direct relationship between hydroxide, carbonate and bicarbonate in concentration, while the proton (H^+) concentration is inversely related to the carbonate and bicarbonate concentration as described by Brady and Weil (1999).

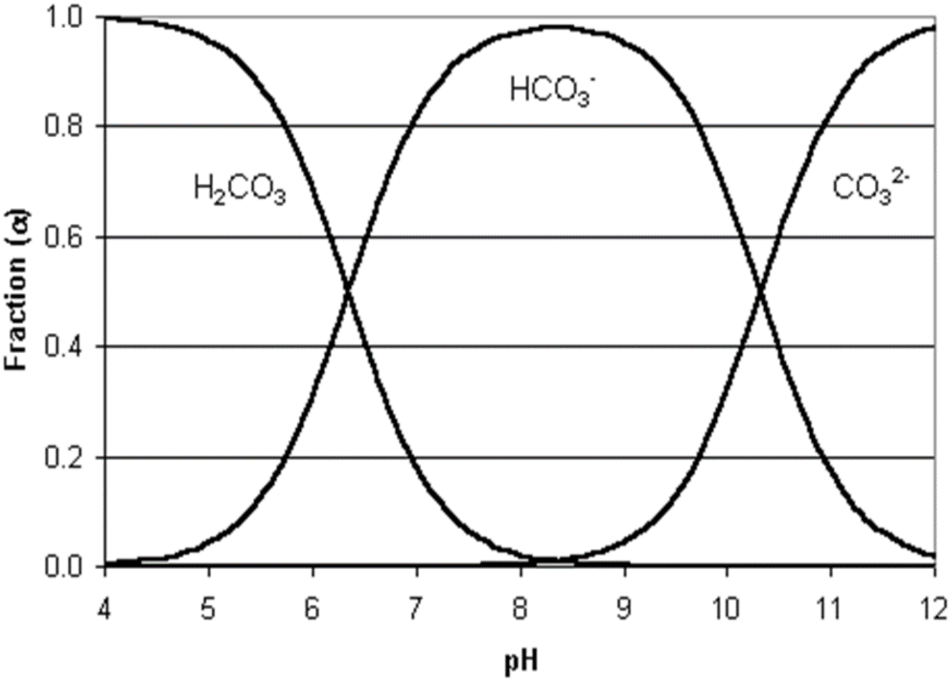

Figure 2.1 Relation between fractions of carbonates in soil (Lindsay, 1979).

Figure 2.2 demonstrates a direct relationship between hydroxide, carbonate and bicarbonate in concentration, while the proton (H^+) concentration is inversely related to the carbonate and bicarbonate concentration as described by Brady and Weil (1999).

2.3.2. Relationships between alkalinity and sodicity

A saline soil dominant with carbonate and bicarbonates is defined as a saline and alkaline soil (Rengasamy, 2016). Alkaline soils can become sodic where precipitation of Ca^{2+} and Mg^{2+} at high pH, via the existence of carbonate anions, results in sodium (Na^+) becoming a dominant ion (Rengasamy, 2010). Generally, saline-sodic soils have a spectrum of disorders and the soil solutions have a range of $EC_e > 4$ dS m^{-1} and an ESP >15 (US Salinity Laboratory Staff, 1954) and ESP > 6 for Australian soils (Northcote & Skene, 1972). Further, saline-sodic soils can become alkaline as the pH of the soil increases above 8.0. Subsequently, these soils become alkaline and carbonate and bicarbonate dominant within the anion complex (Lindsay, 1979; Rengasamy & Olsson, 1991). The combination of a salinity, sodicity and alkalinity in soils leads to potentially much greater adverse impact on soil properties and plant growth limitations, as compared to any of these constraints (i.e., salinity, sodicity, or alkalinity) occurring individually. However, the spatial distribution at fine scale (within a paddock) of saline-sodic and alkaline, non-saline sodic and alkaline soils, and other combinations of constraints, is rarely considered within management regimes. Exacerbating this, in different parts of the world, while the standards are consistently based on the EC and SAR of the soil solution and the pH of the soil, the thresholds for these standards differ for American soils (US Salinity Laboratory Staff, 1954), European soils (Szabolcs & Fink, 1974) and Australian soils (Rengasamy, 2016). For Australian saline, sodic, and alkaline soils, the criteria is based on SAR and EC of the saturation extracts of the soil, and pH measured in 1:5 soil: water suspensions (Rengasamy, 2010).

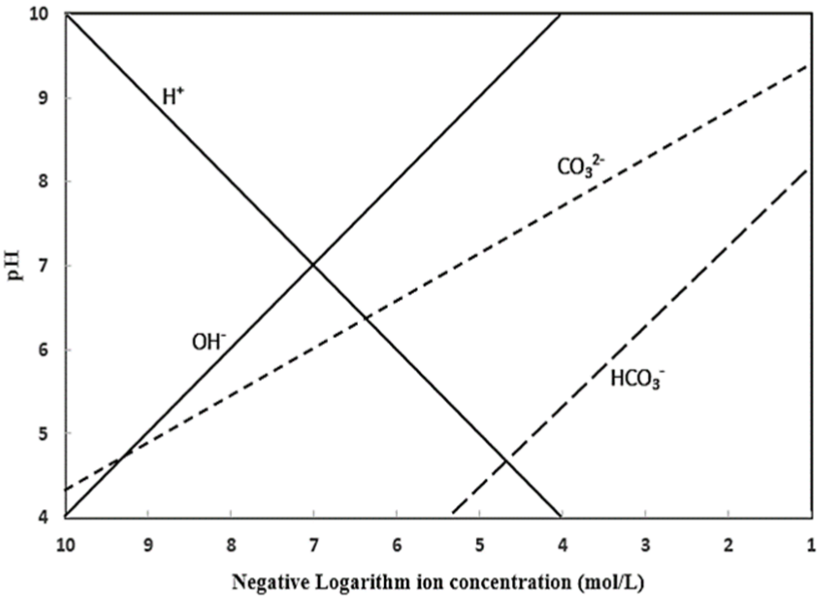

Figure 2.2 Relationship between proton, hydroxide, carbonate and bicarbonate concentrations (Brady & Weil, 1999).

Alkaline soils often coincide with sodicity conditions and dense subsoils, while sodic soils with high SAR solution values might not usually have high alkalinity and pH (Van Beek & Van Breemen, 1973). Calcarosol soils usually have high pH and sodicity (determined as ESP), and their adverse effects on soil physicochemical traits are difficult to distinguish predominantly soil structure breakdown. The saturation paste pH of the solution has shown to be less than 8.3 in many saline and sodic soils that do not contain sodium carbonates (Chorom, 1996). However, Gupta et al. (1984) stated that pH with adjacent association with sodicity of calcarosol soils often affects the whole range of physicochemical and surface properties of soils.

An increase in pH and carbonate anions can cause a significant increase in the ESP (Figure 2.3), due to the fact that base anions increase as pH increases, subsequently resulting in the precipitation of Ca as $CaCO_3$, which consequently amplifies the effect of the Na content within the soil solution and the exchange (Abrol et al., 1980). Studies have shown that the increase in soil ESP can be strongly correlated with increasing pH (Cemek et al., 2007; Li et al., 2007; Minhas et al., 2007), although this depends on the initial conditions of the soil (Figure 2.3B). Figure 2.3 demonstrates that small increases in the pH of soil could result in a large increase in ESP of the soil solution, especially where the pH is above 7.5.

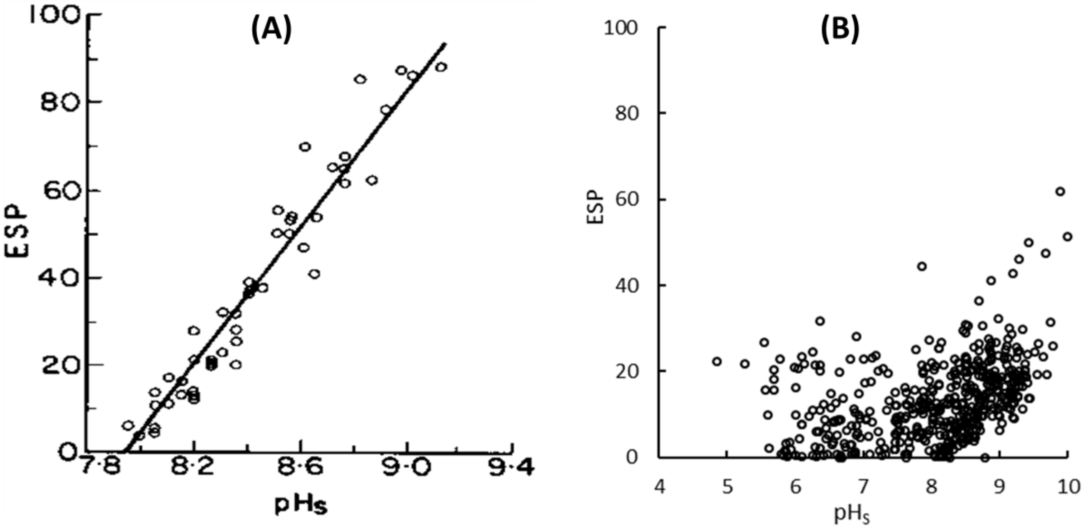

Figure 2.3 Relationship between the pH of the saturated soil paste and the exchangeable sodium percentage for: (A) only for specific kinds of sodic soils having a saturated soil paste pH above 8.0 in Abrol et al. (1980); and (B). 483 soils in the University of Southern Queensland soil database (Bennett, Unpublished Data), with these soils coming from throughout New South Wales and south-eastern Queensland, spanning acidic and alkaline soils and soil textures ranging from sandy clay loam through to heavy clay.

The full collection of soil survey data for inland Queensland does, however, show that there is not necessarily a strong relationship between pH and ESP – due to the widespread presence of pH inversion Vertosols (Biggs, 2006) (Figure 2.4). These soils have an alkaline surface over strongly acid subsoil, but are sodic to strongly sodic throughout (Isbell, 1957; Maher, 1996).

The study of Minhas et al. (2007) found that the increasing alkalinity (presented as RSC) of irrigation water increased the ESP in the soil profile cultivated with a wheat crop, and the affinity was higher with increasing sodium in the irrigation water with and without involvement of rainfall (Figure 2.5). Hence, an increase in pH above 7.5 generally increases the preference of Na^+ for adsorption onto clay colloids (Ezlit et al., 2010). On this basis, it is generally accepted that alkaline soils will have greater ESP, although there are exceptions to this such as described above, and those Vertosols that are derived purely from basalt and are generally non-sodic. However, the dissolution of pedogenic carbonates primarily involves increasing partial pressure of carbon dioxide (P_{CO2}) through the processes of organic matter decomposition and plant root respiration, causing an increase in carbonic acid (H_2CO_3), and subsequently carbonate salt dissolution (Mubarak & Nortcliff, 2010; Qadir et al., 2007a; Robbins, 1986).

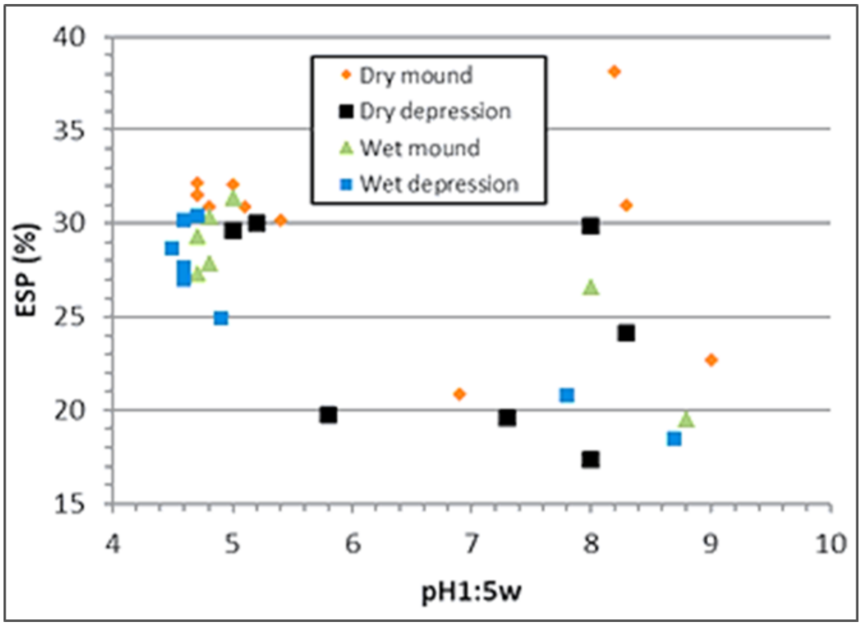

Figure 2.4 Relationship between ESP and pH correlated in most Vertosols with the pH inversion in western Queensland, Australia (Biggs, 2006).

The effect of the soil solution alkalinity also depends on the charge of the clay mineral suite. Suarez et al. (1984) examined the effect of pH values (6, 7, 8 and 9) on clay dispersion (shown as % transmission) and K_s reduction of three soils. Their study revealed that K_s reduced and clay dispersion increased with the increase of pH in two clay soils dominated with montmorillonite and kaolinite respectively. The cation exchangeable capacity of these soils increased by approximately 10% indicating an increase in net negative charge and, most likely, increasing ESP in the system. Likewise, Gupta et al. (1984) indicated increasing pH from 6 to 10.8 for a Na^+ saturated soil resulted in a severe increase in clay dispersion, in particular soils with a high content of illite clay mineral. Hence, the adverse impacts of increased pH on the soil clay dispersion can be driven by sodium and the subsequent effect of this on the net negative charge of the soils.

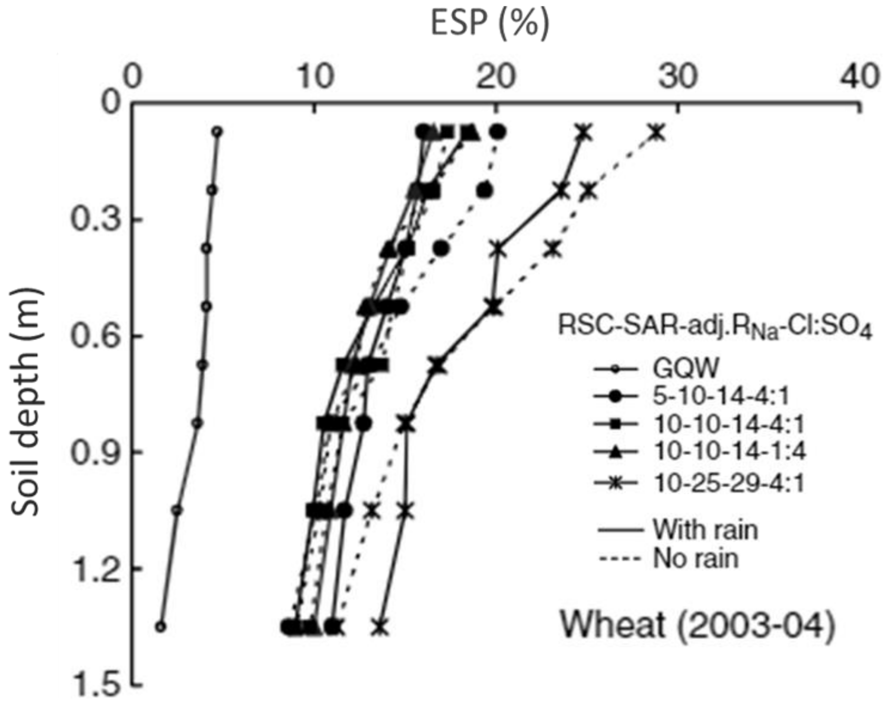

Figure 2.5 Soil depth distribution of sodicity (ESP) in soils irrigated with different alkaline (RSC, residual sodium carbonate) waters and good quality irrigation water (GQW) at the harvest wheat (2003–2004) in study of Minhas et al. (2007) .

2.3.3. Impact of alkalinity on the electrical double layer and electrokinetic properties of soils

2.3.3.1. Diffuse double layer and Zeta potential (ζ-potential)

The nature and strength of interactions between clay particles in contact with soil solution are the result of attraction and repulsion forces (Barzegar et al., 1994; Churchman et al., 1993). The distribution of ions around the clay particle is dynamic and a gradient extending from near the clay surface, developing an electrical double layer (EDL) (Chorom, 1996; Hunter, 1981), also known as the diffuse double layer (DDL) (Sumner, 1992). The clay particle dispersion mechanism is generally agreed to be associated with the thickness of the EDL surrounding individual hydrophobic colloids. The effect of electrolyte concentration and the net charge on clay particles causes dispersion or flocculation of clay particles (considering a colloidal suspension), and controls both the point an aggregate disaggregates from a potential minima, as well as the aggregation-dispersion boundary (Bennett et al., 2019a; Dang et al., 2018a; Quirk & Schofield, 1955). Therefore, solution concentration and clay surface charge describe much of the dynamic in EDL and net attraction and repulsion forces among clay particles in suspension (Chorom &

Rengasamy, 1995; McBride & Baveye, 2002). The magnitude of net repulsive forces depends on the:

1) Net particle charge;
2) Ionic composition suite of the applied/soil solutions; and,
3) Ionic concentration of this same solution.

Chorom and Rengasamy (1995) suggested that the cause of particle flocculation is largely associated with an increase in electrolyte concentration, producing compression in the EDL and higher zeta potential (ζ-potential), with this phenomenon related to clay mineral charge reduction, change of magnitude of variable charges and thus net negative charges. The net negative charge is the primary reason in clay dispersion, and that pH affects clay dispersion by changing the net charge on clay particles (Chorom et al., 1994). Marchuk et al. (2013) revealed that as the pH increases, both turbidity (clay dispersion) and negative zeta potential (reflecting the net charge on clay particles) increase. The ζ-potential resultant values of clay particles can be categorised in terms of the ability to induce clay dispersion, as demonstrated by (Yong et al., 2012) (Table 2.3). In general, Table 2.3 illustrates that the degree of dispersivity of soils increases with decrease in ζ-potential values, and indicates a soil becomes dispersive for ζ-potential more negative than -30 mV (for a negatively charged clay colloid system).

The ζ-potential of most charged particles is dependent on solution pH, ionic strength, types of ionic species, and clay mineral characteristics (Acar & Alshawabkeh, 1993). In general, an increase in pH results in more negative ζ-potential (-mV), resulting in clay dispersion in soils regardless of clay content, mineralogy, organic carbon at different ionic concentration. However, at very high alkaline pH, clay suspensions have been observed to flocculate in Mg and Ca systems (Chorom & Rengasamy, 1995; Chorom et al., 1994). This indicates that the ζ-potential of clay particles is a good indicator for particle electrical potentials: the higher the zeta potential, the higher the surface potential of charged clay particles. Figure 2.6 depicts the zeta potential at the slipping plane between the Stern layer and EDL on a charged particle. It also provides some indication of the pH effect on change in clay particle negative charges and ζ-potential.

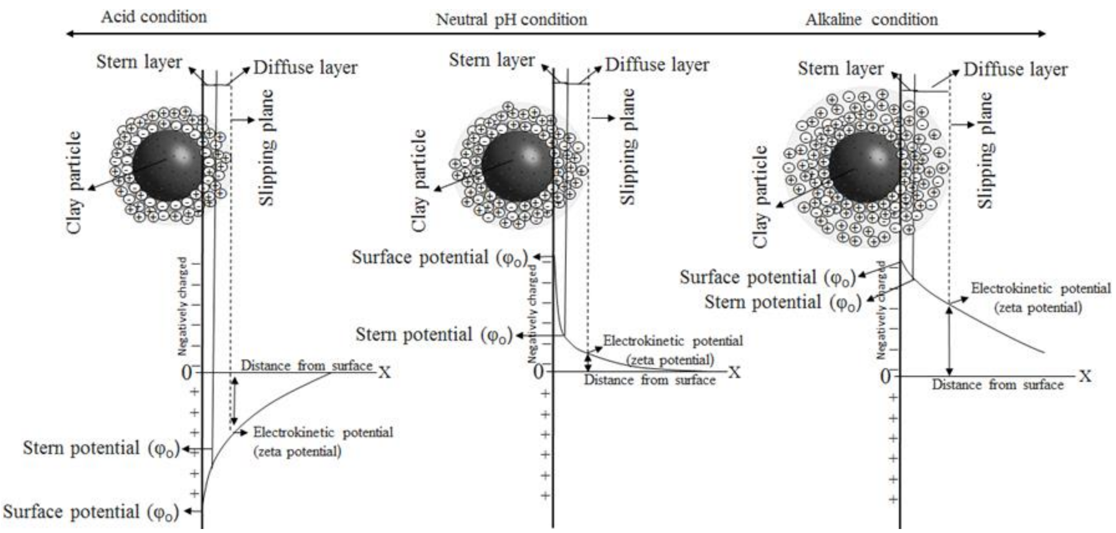

Figure 2.6 Schematic representation of zeta potential under acid, neutral and alkaline conditions. Adapted from Fairhurst (2013).

Table 2.3 Interpretation of soil microstructure condition from the range of zeta potential (ζ-potential) modified from Yong et al. (2012).

Average Zeta Potential (ζ-potential) in mV	*Soil aggregate stability*
+3 to 0	Maximum aggregation and flocculation
0 to -5	Excellent aggregation and flocculation
-6 to -10	Fair aggregation and flocculation
-11 to -20	Threshold of aggregation and slight dispersion
-21 to -30	Slight dispersion
-31 to -40	Moderate dispersion
-41 to -50	High dispersion
-51 to -60	Very high dispersion
< -61	Extremely high to complete dispersion

Change in soil pH results in the increase in net positive and negative charges at low pH and high pH respectively (Chorom et al., 1994). The study of Perrott (1977) confirmed that the increase in pH results in the increase of negative charges and positive charge reduction for their tested soils (Figure 2.7).

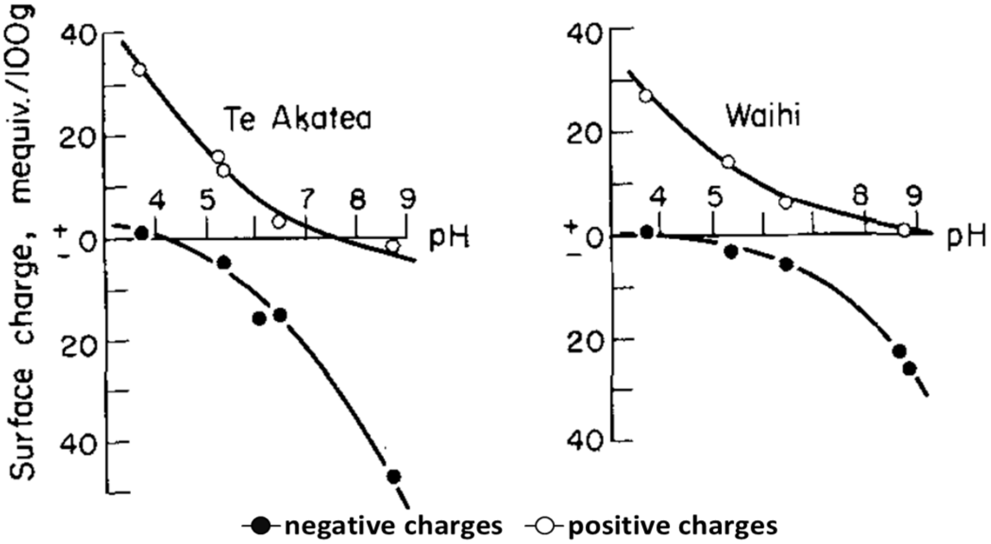

Figure 2.7 Surface charge variation with pH for soil clays (Perrott, 1977).

2.3.3.2. The pH-dependent clay surface charges

Clay particle charges also depend on the protonation and deprotonation of aluminol and silanol groups of clay minerals, which is driven by pH such that increased pH increases negative charge, while acidic pH transfers this charge to positive (Schofield, 1950). However, high activity clays, often correlated with large specific surface area characteristics (Van Olphen, 1977), are largely considered permanently negatively charge (isomorphic substitution determined); protonation and deprotonation processes occur at the clay crystal edges (Van Olphen, 1977) depending on the pH of the solution, with this effect negligible in mineral suites with large edge-to-face contact, or with very high face-to-edge ratio.

Clay crystal structure interruption causes changes in the total surface charges, disturbance of clay platelets, CEC and pH of the soil solution (Oades et al., 1989) and as a result, clay dispersion or flocculation behaviour is also altered. The cation exchange usually depends on the solution pH which is related to the release of hydrogen (H^+) (deprotonation) ions from the edge sites of the mineral and may also take place on the flat exposed planes of the sheets (Miranda-Trevino & Coles, 2003). Suarez et al. (1984) observed that increasing pH resulted in increase in clay dispersion for their soils and reported that could be due to increase in net negative charge and exchange of sodium. At low pHs, the edge-to-face bonding and bonding of positive aluminum and oxides to negative clay surfaces is expected to occur (Van Olphen, 1977). These bondings can obstruct clay dispersion and would result in optimum clay particle flocculation.

The certain clay minerals are isostructural and random isomorphic cation substitution in their structure occur depending on the pH of the solution. These cation isomorphous substitution processes generate surface charge in permanently charged minerals, where a surface charge is independent of pH (Sposito et al., 1999). However, for the variable charge surface, the charge is usually dependent on the pH of the equilibrium solution (i.e. to applied irrigation waters) (Sumner, 1993). Sumner (1993) argues that the change of pH in soil solution has no impact on clay dispersion/flocculation of permanent charge clay minerals. In contrast, for the variable charge clay minerals, the negative charges increase when pH increases above pH_{ZPC} (pH at zero point net charge, where there is an equal number of negative and positive charges on the clay particle surface). While below pH_{PZC} the positive charges are expected to be increased and clay particle surface positively charged results in the soil system flocculation. Figure 2.8 shows the effect of pH in three soil systems that have a permanent, variable and mixed (permanent and variable) charge on clay mineral surfaces. It also illustrates the pH_{PZC} location for different soil solution system for these minerals in the soil system.

Moreover, the effects of pH on the clay dispersion rate likely depends on clay content and clay minerals which cannot be simply expected (Oster et al., 1980; Sharma & De Datta, 1985). Soils usually are heterogeneous containing a mixture of clay minerals, each with different point zero charge and amount of variable charge (Sumner, 1993). Soils with a large number of variable charges are more susceptible to pH effects (Mohan & Fogler, 1997; Suarez et al., 1984). The study of Arora and Coleman (1979) specifically indicated that increasing the pH from 7 to 9.5 resulted in a significant increase in the negative charge and clay dispersion of their soils, and for the specimen clay a maximum dispersion occurred at pH 8.3. Their study further showed that increasing the pH of kaolinite soils from 7 to 8.3 resulted in increasing dispersivity of soils more than any other soil samples, including pure clays of illite, vermiculite, and smectite. Likewise, Goldberg and Glaubig (1987) pointed out that montmorillonite dominant soils were more resilient to pH change than kaolinite dominant soils. Therefore, it is very important to consider the impacts of pH on clay dispersion (depending on clay mineralogy and oxide contents) due to increases in negative charges and a positive charge at high and low pH, respectively.

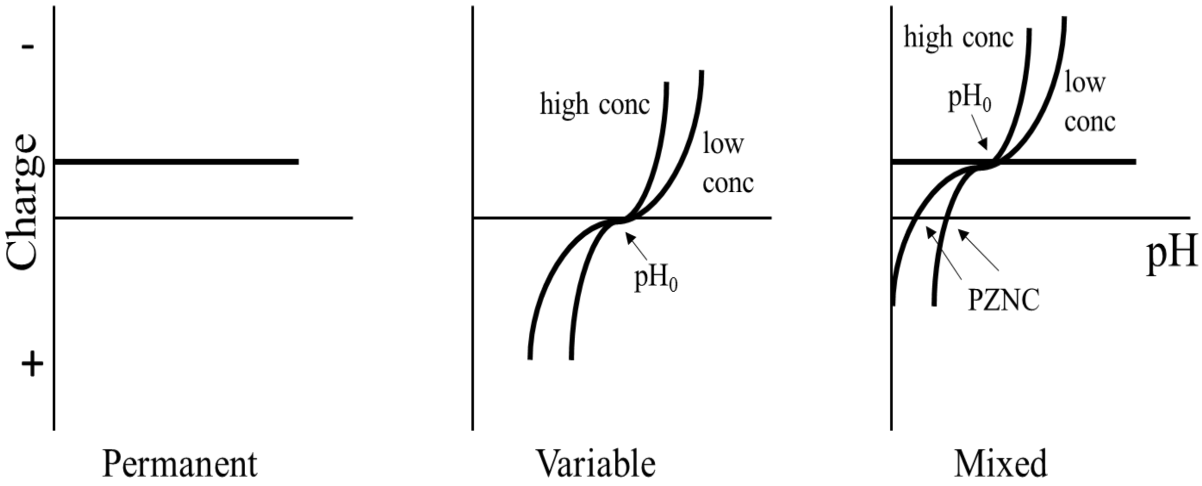

Figure 2.8 Variation in charge with pH and electrolyte concentration of the soil solution for permanent, variable and mixed charge systems. Source: (Sumner, 1992).

2.3.4. Alkalinity and clay mineral response

Clay minerals are very active and have particular properties and reactions that depend on the particle size and net electrical charge discussed in the section above. The effect of alkalinity in increasing adverse effects on soil aggregates is largely dependent on the dominant type of minerals present in the soil. The flocculation-dispersion behaviour of soil clays of different clay minerals is effectively identical (Goldberg & Forster, 1990). The changes in pH have been found to affect disaggregation and dispersion in many pure clay minerals (Arora & Coleman, 1979; Chorom & Rengasamy, 1995; Goldberg & Forster, 1990; Schofield, 1950; Sposito et al., 1992) and in soils with different types of minerals (Gupta et al., 1984; Marchuk et al., 2013; Suarez et al., 1984).

The study of Schofield and Samson (1954) found that the pure sodium montmorillonite and illite suspension dispersed at acidic condition ($pH<7$) while sodium kaolinite suspensions flocculated and kaolinite edge surfaces were positively charged at acid condition ($pH\approx4$). They also stated that kaolinite suspension was totally dispersed at high pH, which was associated with the loss positive charges on the clay particle surface as described in the previous section. In addition, the study of Goldberg and Forster (1990) for the effects of pH and SAR on the clay dispersion of kaolinite, montmorillonite, and illite found that the kaolinite and illite were more affected by change in pH than those for montmorillonite at all SAR values. Likewise, they found that the increase of pH from 6 to 10.8 for sodium saturated soil with a high percentage of illite resulted in an increase in clay dispersion. The study of Chorom and Rengasamy (1995) found the effects of pH on the clay dispersion of pure clay sodium saturated minerals is highly associated with the dominant clay mineral in the order (Na-Kaolinite > Na-illite > Na-montmorillonite) for pH 3.5–9.5 at the absence of electrolyte concentration. For soil clay minerals, the study of Marchuk et al. (2013) demonstrated that the rate of clay dispersion due to the adverse effect of pH depends on the dominant clay minerals, where smectitic soil produced higher dispersed clay and zeta potential compared to kaolinitic and illitic soils (Figure 2.9). Oster et al. (1980) argue that the reasons for the behaviour of soil minerals under change in pH and alkalinity and explain that illite soils are more sensitive to undergo dispersion and clay particle movement than smectitic soils due to the nature of shape and size of illite clay minerals and lower force of edge-to-face attraction. Moreover, Sposito et al. (1992) suggest that the mechanism of illite flocculation and dispersion is affected greatly by the adsorption-desorption reactions of a small quantity of protons on the edge surfaces of suspended particles.

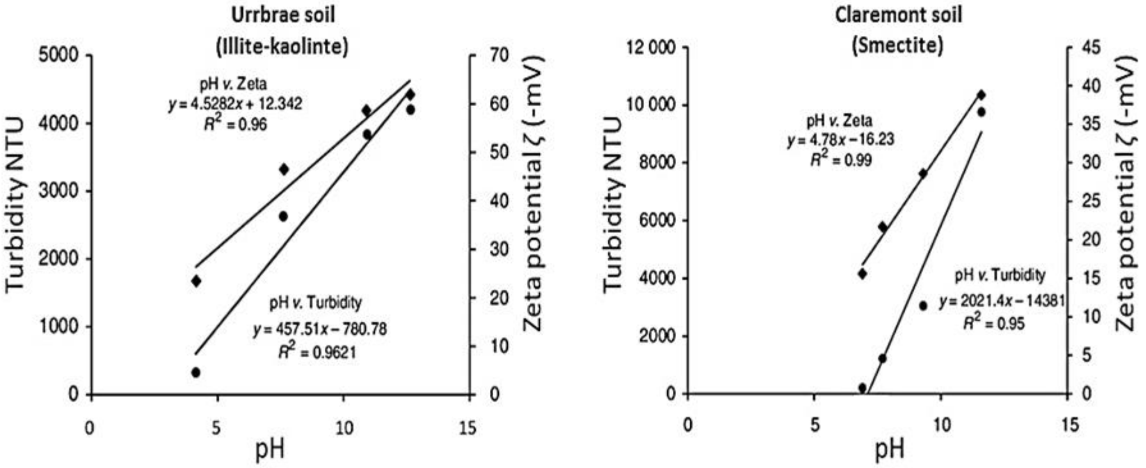

Figure 2.9 Turbidity and zeta potential as a function of the pH in suspension for dominant illite-kaolinite clay mineral soil and dominant montmorillonite soil (Marchuk et al., 2013).

The susceptibility for dispersion due to change in pH is highly correlated to the surface area of clay particles, and the surface area inversely associated to the size of the particle (thickness of the particle). Therefore, the larger clay particles in size have a lower surface area (Brady & Weil, 2008) (Table 2.4). The low surface area clay particle is predicted to be dispersed with a higher rate in comparison to particles with the high surface area even with low exchangeable sodium levels in the system (Rengasamy et al., 1984). This indicates that the behaviour of clay minerals under different levels of alkalinity and pH mainly depends on: i) mineral particle shape and size; ii) specific surface area; and iii) variable negative charges within the clay mineral suite.

However, the existence of aluminum and iron oxides in the soil system will result in lowering the adverse effects of pH on clay minerals and the rate of clay dispersion due to their function as binding agents in the soil structure and increasing resiliency to disperse in soils mixed with different clay minerals (Goldberg & Forster, 1990; McNeal et al., 1968).

Table 2.4 Major properties and characteristics of pH-dependent charge of selected silicate clay minerals and humus (Brady & Weil, 2008).

Colloids	*Type*	*Size (µm)*	*Shape*	*Surface area (m^2 g^{-1})*		*Negative charge*			*Positive charge (cmol$_c$ kg^{-1})*
				External	*Internal*	*Total at pH 7 (cmol$_c$ kg^{-1})*	*Constant (%)*	*Variable (%)*	
Kaolinite	1:01	0.1–5	Hexagonal crystal	5–30		8	5	95	2
Smectite	2:01	0.01–1	Flakes	80–150	550–650	100	95	5	0
Illite (Mica)	2:01	0.2–2	Flakes	70–175		30	80	20	0
Humus	Organic	0.1–1	Amorphous	variable		200	10	90	0

2.3.5. Effect of alkalinity on organic carbon dissolution

Organic carbon (OC) is an important component of a healthy soil that plays a major role in many physical, chemical and biological processes in the soil (Curtin et al., 2016; McDowell, 2003). The OC is well known to improve soil properties through binding clay particles to form a stable aggregates, helps to improve water retention, contributes to cation exchanges, and works as an energy source for soil organisms (Gupta et al., 1984; Helling et al., 1964; Marchuk et al., 2013; Stevenson & Cole, 1999; Tisdall & Oades, 1982). The principal function of organic matter for the soil structure is to act as a binding agent to form wide ranges of aggregate size class in the soil, coating clay particles and forming macro-aggregates (>250 µm) (Lieffering & McLay, 1996; Oades, 1984). The OC content is mostly low in alkaline soils because of the adverse effect of a high alkalinity on the chemistry of soil OC and limitation of agricultural productivity in alkaline soils (McDonald et al., 2017). Spain et al. (1983) indicated that the OC content is negatively correlated with the pH. The solubility of OC is pH dependent and significant increases in the dissolved organic carbon (DOC) have been perceived when pH was increased by the addition a source of alkalinity to soil (Curtin et al., 2016; Tavakkoli et al., 2015). The effects of increasing alkalinity on the solubility of OC are likely to depend on the nature of the alkaline source that causes the alkalinity/increased pH. The solubility of OC can be greater in the presence of monovalent cations (i.e. Na^+, K^+, and NH_4^+) compared to Ca^{2+} and Mg^{2+} cations (Curtin et al., 2016; Nelson et al., 1998). The study of Tavakkoli et al. (2015) found that the application of Cl^- salts of Na^+, K^+, Mg^{2+} and Ca^{2+} reduced the concentration of DOC by 11, 30, 39 and 49% respectively compared with water extracts. Also, the addition of SO_4^{2-} salts of Na^+, K^+, Mg^{2+} and Ca^{2+} reduced the DOC concentration by 4.5, 17, 24 and 42%, respectively. They also indicated that the DOC concentration increased significantly in the presence of HCO_3^- and CO_3^{2-} salts for four Australian soils. Similarly, the study of Marchuk et al. (2013) for four south Australian soils observed that the application of 0.1 M of NaCl and KCl resulted in the different residual OC in the soil ranges from 0.26–2.57% and 0.3–2.9%, respectively for the solution pH ranges 6.6–9.7. Curtin et al. (2016) found that the effects of $Ca(OH)_2$ and KOH on the DOC are similar in acidic conditions ($pH<6$) and the rate of DOC is dependent on the increasing pH for both alkaline solution especially for the addition of KOH (Figure 2.10).

This indicates that increasing alkalinity in the soil solution most likely affects the reduction in OC in the soil system (Sposito, 2008). The effects of hydroxides and pH on DOC, soil disaggregation, and subsequent hydraulic conductivity reduction were identified to be partly associated with reduction in OC in the soil system (Nyamangara et al., 2007; Suarez et al., 1984). Many studies (i.e. Frenkel et al. (1992); Oades (1984); Nelson et al. (1998)) have found that the amount of DOC complex causes an increase the dispersion of clay particles depending on the presence of OC and clay mineralogy. However, the increase in clay dispersion caused by DOC was found to be mainly a result of the adsorption of humic polyanions on the edges of clay particles, which prevent edge-to-face interactions between particles in the soil system (Van Olphen, 1977; Zhang et al., 1991). The studies of Nyamangara et al. (2007) and Lieffering and McLay (1996) have observed a reduction in hydraulic conductivity in soils with different clay contents when leached with NaOH and KOH. They indicated that the DOC from the applied hydroxide solutions increased the clay dispersion in the soil and the movement of dislodged clay particles clogged the pores in the soil, and consequently decreased the soil hydraulic conductivity.

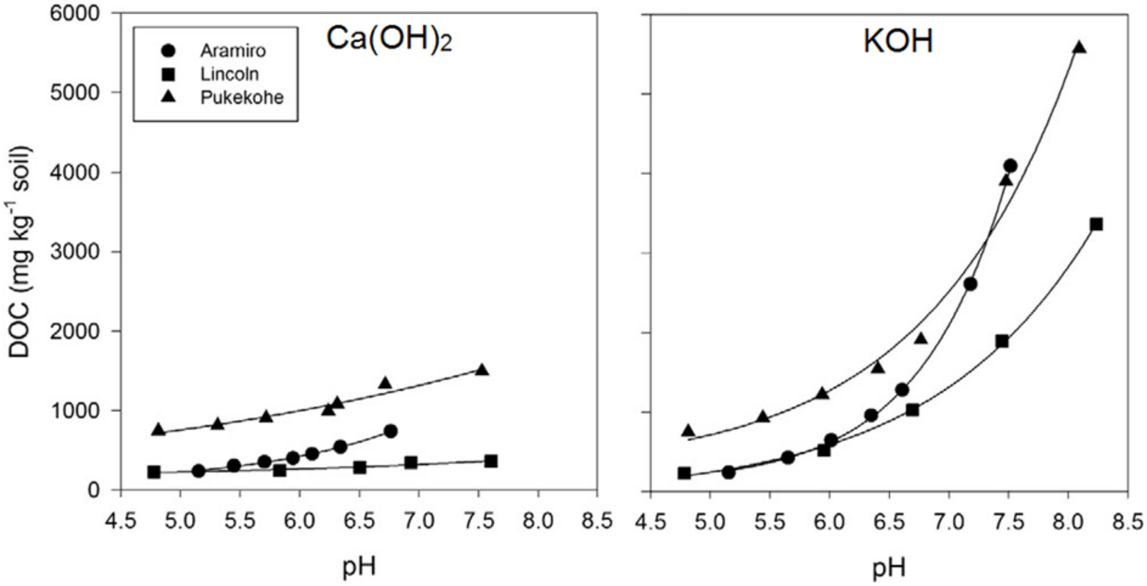

Figure 2.10 Effect of pH on dissolved organic carbon (DOC) using $Ca(OH)_2$ and KOH in three soils (Curtin et al., 2016).

The increase in pH through application of hydroxides, HCO_3^- and CO_3^{2-} appeared to be the most important factors affecting DOC, aggregate stability and hydraulic conductivity reduction, although it depends on the presence of the type of ions in the soil solution system. Therefore, for the suitability evaluation of irrigation water, Suarez and Gonzalez-Rubio (2017) concluded that the pH, salinity, SAR, pH and DOC should be considered the main factors to cause in soil permeability reduction and soil physical properties deterioration.

2.3.6. Impact of alkalinity on soil structure and hydraulic conductivity

Alkalinity has potential effect on the physicochemical properties of soils, due to the presence of precipitated calcium carbonates. Where Ca precipitates in a system containing sufficient Na, and then Na becomes a dominant cation in the soil solution, leading to clay swelling, disaggregation and dispersion. Change in pH of soil solution from an acidic condition to an alkaline pH is believed to cause clay particle disaggregation and dispersion as described by Churchman et al. (1993) (Figure 2.11). Clay swelling, disaggregation and dispersion reduce the soil pore internal geometry (Mace & Amrhein, 2001), meaning that soil solution movement and availability is altered. When swelling and disaggregation pressures exceed attractive forces, the soil disperses, substantially degrading the soil structure stability via surface sealing, slumping and soil pore clogging (Bennett et al., 2019a; Dang et al., 2018a; Levy et al., 2005; McNeal & Coleman, 1966; Quirk & Schofield, 1955; Sumner, 1993). This results in the limitation of solute and water movement in the soil profile and a reduction in hydraulic dynamics.

Hydraulic conductivity is considered as an important soil physical and hydrological property when determining the potential function of soil for agricultural production. The soil hydrological processes change due to different soil physical, chemical and biological processes (Hillel, 2012). It is highly dependent on soil structure, which can be degraded under adverse effect of pH and solute type (i.e. Na, K, alkaline anions and etc.) and their concentrations (Abrol et al., 1988; Levy et al., 2005; Marchuk et al., 2013; Minhas et al., 1999). Changes occur in the composition of the exchangeable ion complex when the water flowing into the soil has a different concentration of solutes than the original soil solution, as the soil exchange and solution chemical suite is considered to be constantly seeking the state of equilibrium (Sposito, 2008). Depending on how the soil solution has changed, significant changes in the hydraulic conductivity and air portions could be expected (Abrol et al., 1988; Buckland et al., 2002; Klute & Dirksen, 1986; Quirk & Schofield, 1955).

A quantitative reduction in soil saturated hydraulic conductivity (K_s) (10–25% reduction) from absolute stability for a given SAR and EC, is referred to as threshold electrolyte concentration (C_{TH}) (Dang et al., 2018a; Ezlit et al., 2013; McNeal, 1974; Quirk, 2001; Quirk & Schofield, 1955). The disaggregation boundary has been suggested as the C_{TH} for the application of saline and sodic marginal quality water. The Department of Natural Resources (DNR, 1997) adopted a concept to determine suitability of irrigation water quality via overlaying its EC and SAR values on generalised C_{TH} curves (Figure 2.12A), and it is used as a standard guideline for assessing the adverse effect of saline and sodic on soil structural degradation in Australian and New Zealand Environment and Conservation Council guidelines (ANZECC, 2000) . Conceptually, water quality that falls to the right of the dashed line is unlikely to cause soil structural problems, while that between the two curves is considered marginal and that to the left of the solid curve would induce a severe reduction in hydraulic conductivity of the soil. However, the soil's response to salinity and sodicity of irrigation water is soil specific (Bennett et al., 2019a; Bennett & Raine, 2012b) (Figure 2.12B). The effects of pH and alkalinity have not been incorporated into the C_{TH}

determination when tested for the suitability of marginal quality irrigation water to dispose on lands.

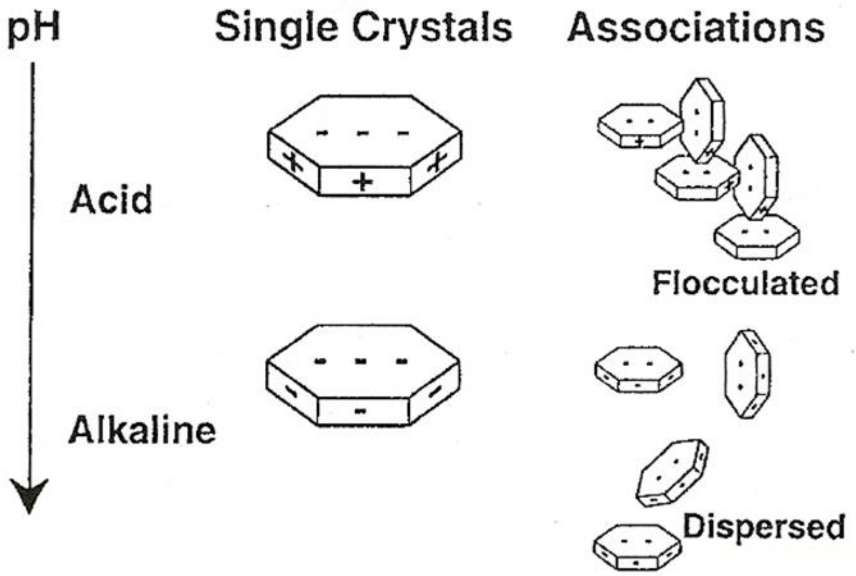

Figure 2.11 Schematic diagram of the effects of pH and alkalinity on clay dispersion (Churchman et al., 1993).

However, alkalinity is another effective factor responsible for increasing sodium concentration of soil solution, which has a correlation with the increasing dispersion of clay particles, and results in hydraulic conductivity reduction (Barrett-Lennard et al., 2016). Permeability restrictions are also associated with the concentration of HCO_3^- and CO_3^{2-} in soils through precipitation as calcium and magnesium salts during the drying process, resulting in increasing the relative proportion of sodium. The increase in Na concentration in alkaline soils leads to extra deleterious soil physicochemical properties, as Shainberg et al. (1992) outlined that any small increase in the amount of exchangeable Na causes considerable effect on clay dispersion, and resulting in lower hydraulic conductivity (Abrol et al., 1988; Frenkel et al., 1978) (Figure 2.13).

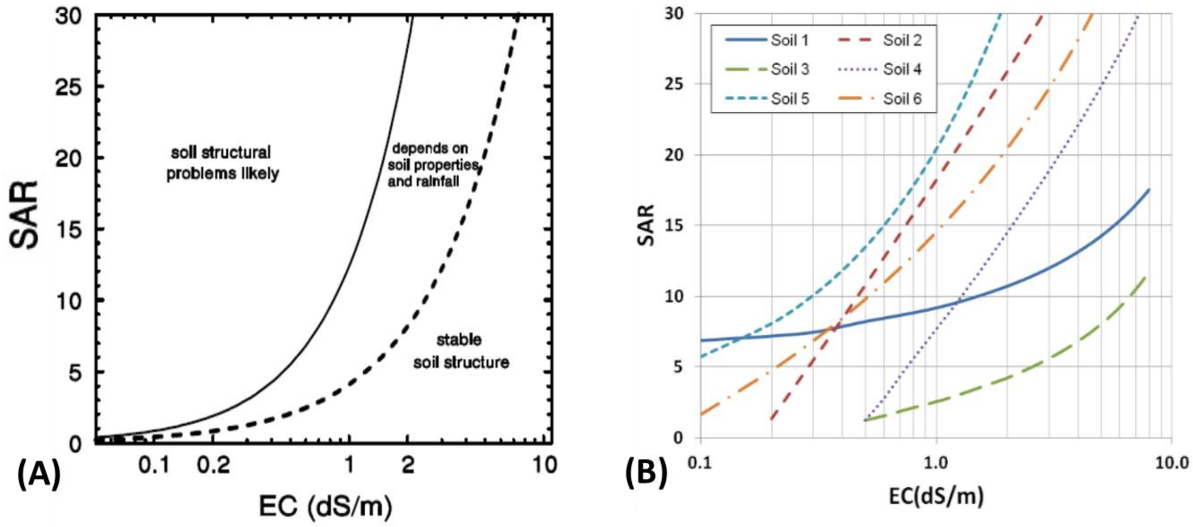

Figure 2.12 The relationship between SAR and EC for soil structural stability determined using threshold electrolyte concentration (*C_{TH}*) (A) (DNR, 1997) and (B) the *C_{TH}* (i.e. 20% reduction in *K_s*) for the Vertosols (Soils 1, 2 and 6) and Chromosols (Soils 3, 4 and 5) soils in Bennett and Raine (2012b).

The study of Candemir and Gülser (2012) for the determination of saturated hydraulic conductivity (K_s) on fine-textured and alkaline soils has found that exchangeable Na at high pH had the highest direct influence on K_s, following in order with clay content, CEC, and EC. In addition, where pH>8.2 and Na is applied with irrigation water, the soil solution SAR would be expected to increase as Ca and Mg in irrigation water are removed due to alkalinity precipitation processes, further causes to the movement of dislodged clay particles into pore spaces and K_s reduction (Carrow & Duncan, 1998; Mashhady & Rowell, 1978; US Salinity Laboratory Staff, 1954) (Table 2.5). Likewise, Suarez et al. (1984) indicated that the K_s values were lower at the solution of pH 9 than at pH 6 for both montmorillonite and Kaolinite clay soils, and these results of K_s were normally dependable with visual transmission (equivalent to Turbidity) measurement of clay dispersion. Subsequently, high pH and alkalinity with a source of sodium present, and low electrolyte concentration of the solution dramatically reduces soil permeability (McNeal and Coleman, 1966) as a result of clay dispersion and pore blockage (Bennett, 2013; Rengasamy & Marchuk, 2011; Shainberg et al., 1981). This trend will increase with the increase of the level of alkalinity of irrigation water with the existence of sodium in irrigation water or in soil solution (Carrow & Duncan, 1998) (Table 2.5). The study of Suarez and Rubio (2010) found that irrigation water of pH 8.2 and comparable with SAR and water compositions resulted in lower infiltration rate than the irrigation water with pH 7.0 and at the same SAR value. Hence, alkalinity causes sodicity to develop, which has deleterious effects on the physiochemical properties and requires proper management strategies to reduce negative effects on soil properties.

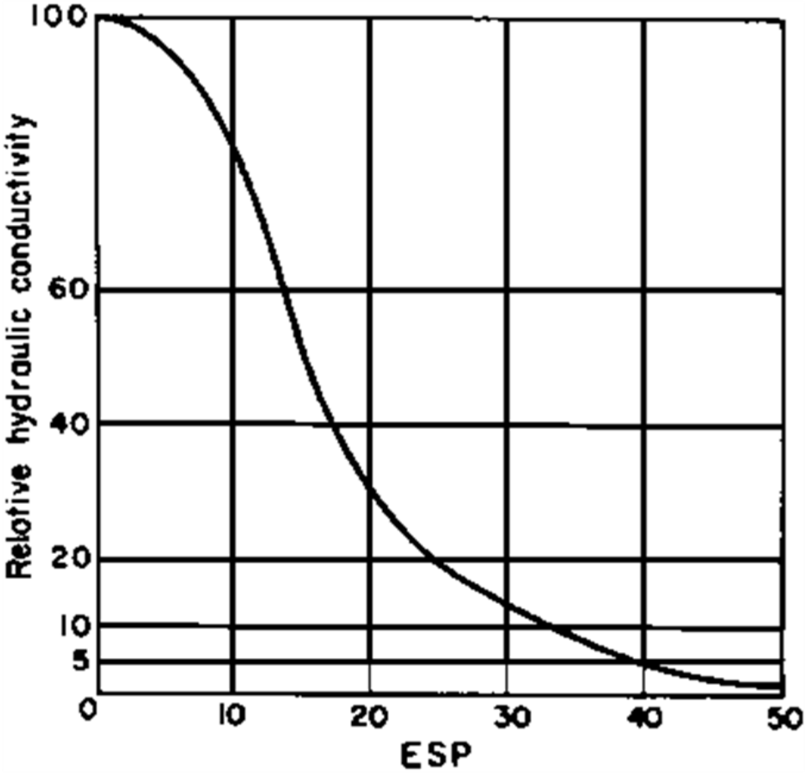

Figure 2.13 Schematic diagram of the relative hydraulic conductivity of soil as affected by increasing ESP (Abrol et al., 1988).

Table 2.5 The potential problems associated with bicarbonate and carbonate modified from (Carrow & Duncan, 1998).

RSC (mmol$_c$ L^{-1})	*Effect classes*	*Sodium hazard*
< zero,	Negative	No hazard, Calcium and Magnesium remain active, and will not be precipitated as carbonate salts.
Zero - 1.25	Low	Some Ca^{2+} and Mg^{2+} will be removed from irrigation water
1.25 – 2.5	Medium	Considerable amount of Ca^{2+} and Mg^{2+} will be removed from Irrigation water
>2.5	High	Most of the Ca^{2+} and Mg^{2+} precipitate as carbonate salts, increasing Na^+ build-up depends on the Na content of water.

2.3.7. Crop responses to alkalinity conditions

Alkalinity is considered a major factor to the agricultural productivity limitation that leads to imposing the root zone constraints in dry land soils of Australia. These limitations in root zones restrict the root system development and finally crop yield (Rengasamy et al., 2003). The root zone constraints include physical and chemical restrictions as well as an essential nutrient deficiency that resulted from a high alkalinity level in the soil. The physical constraints in the root zone comprise soil structural decline caused by increasing exchangeable Na^+ concentration due to alkalinity in the soil (Mashhady & Rowell, 1978; US Salinity Laboratory Staff, 1954). The deterioration of the soil structure results in surface sealing and crusting, and following to poor water and air movement within soil layers restricting water storage and drainage (Amezketa et al., 2005), this phenomenon leads to lack of oxygen to maintain respiration of plant roots and low available water. The precipitation of carbonate salts and maintaining high pH are the major factors to decrease the availability of essential nutrients for plants in alkaline soils. The alkalinity of water is considered critical among other factors because of its direct and indirect effects on plant growth, and direct impact on growing solution pH and high exchangeable sodium (ESP) (Kuehny & Morales, 1998).

Plants respond to carbonate ions (HCO_3^- and CO_3^{2-}) concentration with foliage growth that is associated with a drop in a number of leaves, dry mass, and foliage elongation. Plant foliage reduction is potentially attributed to a low photosynthetic rate occurring in the HCO_3^- affected chlorotic leaves (Bernstein, 1975). The Leucaena foliage was very sensitive with necrosis and chlorosis evident through reduction of relative shoot fresh mass and chlorophyll fluorescence when saline-sodic and alkaline water applied at EC greater than 3.0 dS m^{-1} and containing more than 500 mg L^{-1} of $CaCO_3$ as shown by the study of (Cicchelli et al., 2016). Lal et al. (1980) also found that the grain and straw of wheat and barley yields decreased when irrigation water applied with RSC up to 9.5 $mmol_c$ L^{-1}. Moreover, the higher sodium uptake was observed with the reduction of phosphorus, potassium, calcium at high levels of RSC in irrigation water. Similarly, Choudhary et al. (2006) have achieved a poor yield of a sunflower crop when alkaline and sodic groundwater having RSC of 10 $mmol_c$ L^{-1} was applied for six years as a result of a build-up of sodium in soil, an increase of pH and ESP of the soils as well as a decrease in infiltration rate. The accumulation of sodium ions in the soil can also affect the stomatal closure, and obstruct water loss in plants

(Bernstein, 1975). The cotton and wheat yields also were lower in sodic and alkaline irrigation water than fresh water and gypsum applied soils, indicating negative effects of high Na^+ in irrigation water when used with the absence of management approach (Murtaza et al., 2006). These results show that the use of alkaline and sodic irrigation water and the number of irrigations throughout the season and over the years increases the alkaline salt accumulation and sodium saturation of the soil and crop yield reduction (Bajwa & Josan, 1989).

Alhendawi et al. (1997) stated that the root length of barley, sorghum, and maize depressed with the increase of HCO_3^- concentration in solution; but the root diameter developed in response to increasing concentration of HCO_3^-. They suggested that the rapid decline in foliage growth signal is observed to be associated with the root growth restriction. Even though, there is clear differences in tolerance of some species of plants for alkalinity and sodicity such barley (Lal et al., 1980), this underlying proper mechanism in alkalinity tolerance have been suggested for some species of plants. These effects depend on the plant species due to their sensitivity to alkalinity and sodicity level soil and applied irrigation water (Cicchelli et al., 2016; Lal et al., 1980). Thus, as the excess accumulation of alkaline carbonate salts in the soils results in the degradation of soil physical and chemical properties as well as harms plant growth, it is necessary to reduce the quantity of carbonates to a normal level so as to avoid deterioration of soil properties and improve plant growth.

2.4. Management implications considering alkalinity

The management of alkalinity is generally achieved with the use of amendments. Most of the alkaline soils contain sufficient quantities of extremely low-solubility calcium carbonate nodules, which does not supply a sufficient amount of Ca^{2+} compared to other chemical amendments such as gypsum (Qadir et al., 2001a). Amendments are either added to irrigation waters or applied directly to the soil surface. There are several options to ameliorate alkalinity of soil and irrigation waters such as chemical, and traditional agronomic methods (sowing tolerant plants). Chemical amendments as a source of calcium and acid-forming materials are added to bring the alkalinity to a desirable level. It is crucial to assure that management is suitable to maintain the soil resource and fulfill agricultural production. Given the nature of this work, only sulphur and gypsum based ameliorative process are discussed below.

2.4.1. Amelioration of soil alkalinity

2.4.1.1. Amelioration through sulphur application

Traditionally, the variety of sulphur sources have been used successfully to treat alkaline soil and to neutralise pH and thus to reduce alkalinity (Barrett-Lennard et al., 2016). The acid-forming chemicals such as elemental sulphur (S), lime sulphur (CaS_5), pyrite (FeS_2), ferrous sulphur ($FeSO_4$), and sulphuric acid which can be applied based on the availability of these products and the degree of alkalinity. In soil, sulphur is oxidised by soil microorganisms to form sulphuric acid which has the potential ability to convert carbonates and increase availability of Ca in the soil system (Bohn & Westerman, 1971; Waksman & Joffe, 1922). It has also been suggested that sulphuric acid can be directly applied to the soil to increase the solubility of Ca^{2+} and the ionic strength of acidic solutions, via reaction with calcite in an open reaction, producing water molecules and releasing CO_2 to the atmosphere (Equation 2.5) (Miyamoto & Stroehlein, 1986; US Salinity Laboratory Staff, 1954).

$$H_2SO_4 + CaCO_3 \leftrightarrow Ca^{2+} + SO_4{}^{2-} + CO_{2\,(gas)} + H_2O \qquad \textbf{Equation 2.5}$$

2.4.1.2. Amelioration through gypsum application

Gypsum is traditionally considered an efficient amendment to reduce the effects of sodium in sodic and alkaline soils where affected by alkalinity and sodicity (Qadir et al., 2001a), as calcium in gypsum exchange for sodium in soils resulting in lowering the SAR and Na exchange sites. Sulphur ions, from gypsum, also oxidise within soils to form sulphuric acid, and reduce the concentration of carbonates, lowering soil pH, and maximising the availability of calcium ions via increasing calcium carbonate solubility (Amezketa et al., 2005; Mace et al., 1999). However, this is an inefficient process as much of the Ca can be lost to precipitation prior to reducing the pH.

Mace et al. (1999) outlined that gypsum and sulphuric acid result in lower sodium adsorption ratio, more soluble Mg^{2+} and Ca^{2+}, and lower pH. The gypsum application at the rate of 15 g kg^{-1} to the soil was documented to reduce the pH from 9.38 to 7.9, reducing SAR from 11.6 to 1.2, and increase Ca^{2+} and improvement in hydraulic conductivity (Chorom & Rengasamy, 1997) (Figure 2.14). Similarly, Fahu et al. (2006) found that pH and SAR of soil solution decreased, and K_s

increased by 37% when gypsum was applied at a rate of 0.5% by soil volume in compare to the control (zero gypsum).

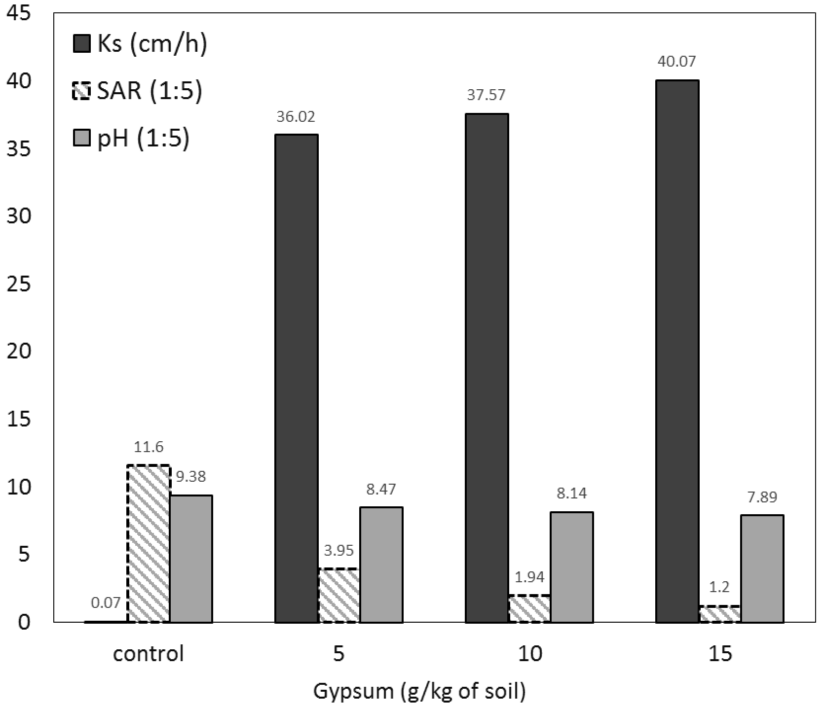

Figure 2.14 The effect of gypsum on improving hydraulic conductivity adapted from Chorom and Rengasamy (1997). SAR is a sodium adsorption ratio, K_s is saturated hydraulic conductivity and pH of the soil solution.

Sodium removal from the soil is essential in improving soil structure stability (Davies & Lacey, 2010; Rengasamy & Olsson, 1991) via exchanging sodium as well as preserving complimentary osmotic pressure in sodic and alkaline soils (Rengasamy & Olsson, 1991). Gypsum improves the structural stability of top layers of soils quickly but it requires several years to reach subsurface layers, while most of the crop roots are present in the upper 40 cm of the soil profile (Davies & Lacey, 2010). The amount of gypsum required is entirely associated with the degree of alkalinity and sodicity of soils and irrigation waters (Qadir et al., 2001b).

Stoichiometric quantities of sulphur and gypsum amendments can be used to neutralise the alkalinity and reduce the sodicity respectively. Bennett et al. (2016b) showed that sulphur application along with gypsum preserved pH and alkalinity concentration of soil and neutralised the alkalinity of untreated coal seam water applied to a red Vertosol. Moreover, soil solution pH of the well-buffered soil remained stable under the sulphur application regime imposed, indicating biological acid generation coordinated the application rate of the alkaline water (Bennett et al., 2016b; Ganjegunte et al., 2008; Johnston et al., 2008; Johnston et al., 2013; Vance et al., 2008).

2.5. Current approaches to modelling alkalinity interactions

Mathematical modelling has become an efficient tool to investigate water flow, solute movement in the soil profile under irrigation. The models investigate various equilibrium chemical reactions between major ion equilibrium and kinetic non-equilibrium chemistry, for instance, ion complexation, cation exchange capacity and precipitation of salts. The use of models is acknowledged to be a practical technique to evaluate the appropriate management for irrigation water qualities, such as sodicity and salinity. However, in the most available model, alkalinity as important soil and water chemical properties have not clearly been documented in chemical reactions, particularly buffering capacity soils and irrigation water are ignored. The HYDRUS-1D (Šimůnek et al., 1998) and PHREEQC (Parkhurst & Appelo, 1999) are two main mathematical models that have been focused on in this study as they have been relatively widely used to consider the interaction between soil physical and chemical properties.

2.5.1. The HYDRUS-1D model

HYDRUS-1D is a finite element for simulating water, heat and solute movement in one-dimensional variability saturated media. This program solves the Richards equation (Richards, 1931) for variability saturated water flow and heat and solute transport using advection-dispersion type equations. It is considered that the presence of monovalent cations often lead to clay swelling, dispersion and poor soil physical properties such as hydraulic conductivity, infiltration rate and soil water retention due to clay swelling and dispersion. The McNeal (1968) model has been utilised to predict clay swelling as a result of the effect of sodicity on soil hydraulic conductivity. In addition, the effect of pH on the soil hydraulic conductivity was calculated from the experimental data of Suarez et al. (1984). This model only includes the reduction functions for some soils of California in United Stated of America from experimental data of McNeal (1968) and Suarez et al. (1984), and assumes that the reduction function values for saturated conditions can be applied to the wide range of pressure heads. The scaling parameter depends on the salt concentration, the exchangeable sodium percentage and pH of the soil of the soil solution. The scaling parameter (r) is involved in the hydraulic conductivity function (Equation 2.6):

$$K(h, pH, SAR, C_o) = r(pH, SAR, C_o)\ K(h)$$ **Equation 2.6**

where C_o is the total salt concentration, h is hydraulic head, and r is the scaling parameter which represents the effects of solution composition on the hydraulic conductivity. The value of r equals to 1 represents the soil chemistry supports a maximum hydraulic conductivity. Then, the scaling parameter is divided into two parts (Equation 2.7):

$$r(pH, SAR, EC) = r_1(SAR, EC)\ r_2(pH)$$ **Equation 2.7**

where r_1 indicates the effects of exchangeable sodium and concentration of salts on the hydraulic conductivity, while r_2 reflects the effects of solution pH on the hydraulic conductivity. The assumption is that the scaling parameter r can be applied for the entire range of pressure head for unsaturated conditions.

2.5.2. The PHREEQC geochemical model

The PHREEQC model is another geochemical program is used for modelling leachate transport and exchange flows. This program evolved from the Fortran program PHREEQE developed by Parkhurst et al. (1980), then later modified to PHREEQC by Parkhurst and Appelo (1999). This program is basically an equilibrium code with the ability to model reactive transport through porous media in one dimension. PHREEQC can perform a wide variety of chemical calculations ranges from speciation to inverse modelling. It implements different phases such as water, gas, mineral and soil solution, ion exchange equilibria, mole transfer of reactant, pressure and temperature changes. This is one-dimensional transport calculation with either reversible or irreversible reactions. The inverse modelling that is useful to determine the initial water chemistry from water composition is another important feature of PHREEQC. In this model, alkalinity is expected to change with pH and carbon, and an equation is included in the inverse model.

The alkalinity of the solutions is controlled by the pH and assumes that the solutions are in equilibrium with atmospheric carbon dioxide (Berner et al., 1983), and it is a minor contributor to control balance. In this model, alkalinity and/or total carbon can be listed in solution input. Then, the pH is accustomed to reach specified alkalinity whether alkalinity and total carbon are specified. It is well documented in the literature that high concentration of carbonate ions are the major causes for the Ca^{2+} and Mg^{2+} precipitation as carbonate salts and the relative fraction of Na^+ is increased (Mashhady & Rowell, 1978). Therefore, the sodicity is another indirect parameter to alkalinity and can be evaluated in terms of the reduction in soil K_s, which can be as a result of clay swelling and dispersion (Agassi et al., 1981; Quirk & Schofield, 1955). The assessment of the impact of sodicity of soil and marginal irrigation waters on the physical and chemical properties of soils and their management can be undertaken through experiments and the use of common mathematical models such as HYDRUS, PHREEQC and UNSATCHEM. There are a number of mathematical computer program models that can be used to simulate solute transport and reactions in soil but only the UNSATCHEM and HYDRUS-1D models include a function that simulates the influence of soil chemistry on hydraulic conductivity.

The management practices for the use of saline and sodic on the physiochemical properties of soils and gypsum and other treatment application have been efficiently predicted using HYDRUS-1D (Jakubowski et al., 2014; Reading et al., 2012; Shaygan et al., 2018; Wang et al., 2016). HYDRUS-1D Versions 4.0 and higher provide support for the coupled HYDRUS-1D with a biogeochemical model PHREEQC (HP1) multicomponent transport model (Jacques & Šimůnek, 2005).

2.6. Conclusions and further research

There is increasing pressure for the use of marginal quality irrigation water due to the limitation in freshwater resources and increasing industrial by-product wastewaters (i.e. CSG water) in Australia, USA and other parts of the world. The use of marginal water quality has the potential to significantly affect physical and chemical soil properties when irrigated with alkaline water. This is because alkalinity along with sodicity of irrigation water induces physical separation of particles due to the repulsion force which results in soil dispersion, pore blockage, aggregate swelling, platelet movement, and organic matter dissolution, and subsequently hydraulic conductivity reduction. The clay dispersion and swelling are the primary processes responsible for soil structural degradation. Hence, the use of marginal and poor quality water requires an appropriate management regime.

The management of alkaline irrigation water is usually carried out with the use of acid-forming materials. The amendments are generally added to the irrigation water or directly applied to soils to enhance soil structure or address the alkalinity of applied irrigation water. The acid-forming materials such as gypsum and sulphur have often been successfully used to reduce the risks caused by alkalinity and sodicity. The strategic management of alkaline and sodic water and soils are important to assure the maintenance of physical and chemical soil properties and thus agricultural productivity.

The current mathematical models have been used to simulate the adverse effects of alkaline irrigation water on the soil properties, and associated management practices. The effects of alkalinity and pH on the soil hydraulic conductivity reduction has been presented in the UNSATCHEM and HYDRUS models through predicting the effects of chemical conditions on the soil physical properties. The effects of pH and sodicity were incorporated into these models as a hydraulic conductivity reduction that considers clay swelling (McNeal, 1968) and pH of applied solution (Suarez & Šimůnek, 1997). These models have been previously used as management tools to simulate the changes in physical and chemical soil properties for sodicity issues. However, there has been very limited research using these models, and the assumptions for hydraulic conductivity reduction have not been evaluated for different soils. Therefore, the validation of these models are required before they can be used to investigate the effects of solutes and reactions and management options for alkaline conditions.

This literature review has highlighted significant research gaps in current understanding of chemical and physical soil behaviors under alkaline conditions that need to be addressed in order to develop appropriate models and guidelines for the management and the strategic use of alkaline irrigation water on wide varieties of soils. Specifically, this research aims to address the current issues and to

- Evaluate the adverse effects of alkaline irrigation water on soil structure degradation, clay dispersion and change in electrokinetic properties of originally alkaline, neutral and acidic soils.

- Globally, the majority of research in this area has been performed for a limited number of soils and therefore there is a need to validate that the increase in pH/alkalinity of irrigation water does indeed cause structural breakdown for an extensive range of soils.
- Identify the effect of irrigation water alkalinity on the soil hydraulic conductivity reduction incorporation with different levels of sodicity and salinity using the current disaggregation model of Ezlit et al. (2013).
- Assess of the effectiveness and ability of acid-forming amendments to neutralise the alkalinity of irrigation water under alkaline soil conditions.
- Improve and expand the current hydraulic reduction function in UNSATCHEM and HYDRUS models to ensure the soil-specific response.
- Review the ability of the current HYDRUS model able for land management strategies and to predict the change in soil physical and chemical properties of original alkaline, neutral and acidic pH from Australia as affected by different levels irrigation water alkalinity.
- Develop a precise and robust model using the wide range of soils to predict reduction in soil hydraulic conductivity reduction due to the effect of pH of the irrigation water for UNSATCHEM and HYDRUS models.

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3. General methodology

3.1. Introduction

The work reported in this thesis consists of a number of distinct experimental studies. Although each experiment has a separate methodology depending on the nature of the study, many of the materials and methods were somewhat similar. This chapter describes the general material and methods in greater detail than the methodologies of each chapter, which are written in the style of journal articles on the basis this is a thesis largely by publication. The specific methodological details for each experiment are described in the relevant chapters.

3.2. Soil selection and sampling

Ten different soils were selected in this study to examine the effects of alkalinity and pH of irrigation water at different levels of sodicity and salinity on the soil stability and hydraulic dynamic changes (Table 3.1). The selected soils were sampled from Queensland and New South Wales states in Australia, and are all commonly found in Australia. These soils were collected from the 0–30 cm depth, and are distinctly different in their soil order, clay mineralogy, texture, structure, pH, alkalinity, exchangeable ions, and dispersivity. The soil order, geographical location and climatic conditions of the regions the soils were sampled from are presented in Table 3.1, and physical and chemical details of the soils used for each experiment are presented in the relevant chapter and in following collection, the soils were dried by spreading them out in a thin layer on a plastic sheet within the laboratory for about two weeks. The air-dried soils were gently then crushed by hand to pass through a 2 mm sieve; care was taken to not apply excess energy in order to maintain the physical bonds of the aggregates <2 mm as best possible. After crushing, the soils were kept sealed in plastic buckets for assessments as presented in this study.

3.3. Soil chemical measurement

3.3.1. Soil pH

Soil pH was determined on a 1:5 soil: water extract. Eight grams of soil were placed into a 50 mL falcon tubes and 40 mL of deionised water were added. The tube was then put on an end-over-end shaker for 1 hour and samples were allowed 20–30 minutes for the soil to settle. The pH of samples was measured based on the method of Rayment and Lyons (2011) (Method 4A1). The determination of pH was carried out using a Radiometer analytical MeterLab® ION450 standard pH meter with a manual temperature calibration on a 25°C basis.

Table 3.1 Location, elevation and climate and land condition of the selected soils

Soil	*Site name*	*Australian taxonomic class*	*Geographical coordination*	*Elevation (m)*	*Mean annual rainfall (mm)*‡	*Site condition*
Wariven	Wariven, NSW	Brown Dermosol	28°58'29"S, 150°26'38"E	305	650	Cultivated, cereal crops
Eldorado	Eldorado, NSW	Red Dermosol	28°54'51.90"S, 150°16'32.21"E	253	640	Cultivated, cereal crops
Moonie	Moonie, QLD	Grey Vertosol	27°49'50"S, 150°9'13.9"E	265	620	Uncultivated, grazing
Dalby	Dalby, QLD	Black Vertosol	27°01'12"S, 151°10'1.2"E	342	670	Cultivated, cereal crops
Greenmount	Greenmount, QLD	Brown Vertosol	27°48'32.8"S, 151°54'22.2"E	520	820	Uncultivated, grazing
St George	St George, QLD	Red Kandosol	27°58'8.4"S, 148°22'51.6"E	210	516	Cultivated, cereal crops
Maryborough	Maryborough, QLD	Grey Kurosol	25°21'36"S, 152°44'40.44"E	28	1051	Uncultivated, Eucalyptus tree
Gatton	Gatton, QLD	Yellow Chromosol	27°35'44.9"S, 152°18'20.1"E	132	770	Uncultivated, grazing
Beerwah	Beerwah, QLD	Grey Chromosol	26°51'19.3"S, 152°59'23.46"E	27	1007	Uncultivated, pine tree
Yarrandoo	Dalby, QLD	Black Vertosol	27°13'46.16"S, 151°19'11.12"E	349	670	Cultivated, cereal crops

‡ mean value of annual rainfall for the last 10 years based on the Bureau of Statistics (BOM), Australia.

3.3.2. Electrical conductivity (EC)

Soil electrical conductivity (EC) was determined using the same 1:5 soil: water extract used for the measurement of pH based on the method of Rayment and Lyons (2011) (Method 3A1). EC was measured using a Radiometer analytical MeterLab® conductivity meter with automatic temperature calibration on a 25°C basis.

3.3.3. Alkalinity (Titration method)

Soil alkalinity was determined using the same samples used for pH and EC determination. The tubes were centrifuged at 3500 rpm for 30 minutes. The soil solutions were decanted into separate falcon tubes (50 mL) for alkalinity measurement. Decanted solutions were titrated with 0.1 M hydrochloric acid (HCl) to reach the endpoint of pH=4.5 using a Radiometer Analytical Titrator (TIM845, Titration Manager). The total calcium carbonate was calculated using Equation 3.1.

$$CaCO_3 = \frac{v_i \times C_{reg}}{V_s} \times c$$ **Equation 3.1**

Where calcium carbonate is in mg L^{-1}, v_i is the added volume of acid (HCl) in mL, C_{reg} is the concentration of the acid (0.1 M), *c* is a conversion factor (50000 for $CaCO_3$; the equivalent weight of CaCO3 is 50, the milligram equivalent is 50,000) and *Vs* is the sample volume in mL.

3.3.4. Soluble and exchangeable cation measurement

Soluble and exchangeable cations were based on method 15A2 from Rayment and Lyons (2011). For soluble ion measurement, 8 g of air-dried soil was weighed, transferred to a falcon tube (50 mL) with 40 mL of deionised water (EC = 5 µS cm^{-1}, pH = 7) and shaken for 1 hour. The falcon tubes were then placed in the centrifuge (SPINTRON, GT-20, Australia) for 30 minutes at 3000 rpm. The supernatant was transferred to another 50 mL falcon tube. The soluble solution was then diluted to a 1:10 ratio (solution: deionised water) to determine the soluble cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+). The soils were retained for measuring exchangeable cations.

To measure the exchangeable cations, 40 mL of ammonium chloride (NH_4Cl 1M) was added to soil sample (initially 10 mL was added, and the tube was shaken by hand, the last of 30 mL subsequently added). These were mechanically shaken for 1 hour. The samples were left overnight and then placed in the centrifuge for 10 minutes at 3000 rpm, with the supernatant transferred to another 50 mL falcon tube. The decanted solutions were then diluted to a 1:20 ratio (solution: deionised water) to determine exchangeable cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+).

The soluble and exchangeable cations were both analysed by inductively coupled plasma atomic mass spectroscopy (Perkin Elmer Nexion ICP-MS).

Cation exchange capacity ($cmol_c\ kg^{-1}$) was calculated as equal to the sum of the exchangeable cations (Brady & Weil, 2008) (Equation 3.2).

$$CEC\ (cmol_c\ kg^{-1}) = \sum Exch.\,(Ca^{2+}, Mg^{2+}, Na^+, K^+)$$ **Equation 3.2**

Soluble cations were used to calculate sodium adsorption ratio (SAR) proposed by Richards (1954) and the cation ratio of soil structural stability (CROSS) developed by Rengasamy and Marchuk (2011) as shown in Equation 3.3 and Equation 3.4, respectively. Exchangeable cations were used to calculate exchangeable sodium percentage (ESP) proposed Richards (1954) and exchangeable dispersive percentage (EDP) developed by Bennett et al. (2016a) are presented in Equation 3.5 and Equation 3.6, respectively. Soluble and exchangeable ions are expressed in units of ($mmol_c\ L^{-1}$)$^{-0.5}$ and ($mmol_c\ kg^{-1}$)$^{-0.5}$, respectively. The unit measurement of SAR and CROSS is ($mmol_c\ L^{-1}$)$^{-0.5}$ and ESP and EDP are in percentage.

$$SAR = \frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}}$$ **Equation 3.3**

$$CROSS = \frac{[Na^+] + 0.56[K^+]}{\sqrt{\frac{[Ca^{2+}] + 0.6[Mg^{2+}]}{2}}}$$ **Equation 3.4**

$$ESP\ (\%) = \frac{[Na^+]}{CEC} \times 100$$ **Equation 3.5**

$$EDP\ (\%) = \frac{[Na] + 0.556[K] + 0.037[Mg]}{CEC} \times 100 \qquad \textbf{Equation 3.6}$$

3.3.5. Soil organic carbon

Air-dried soils were crushed to pass through a 500 μm sieve. The soil organic carbon (SOC) was determined following the rapid wet oxidation method (Walkley & Black, 1934). One gram of air-dried soil sample (moisture content was corrected for) was weighed and transferred into a 500 mL conical flask. Ten mL of 1 N $K_2Cr_2O_7$ was accurately added and gently swirled the flask to disperse the soil in the solution. A volume of 20 mL of concentrated H_2SO_4 was added into the suspension and immediately swirled within the flask until the soil and the reagent were well mixed. A further volume of 200 mL of deionised water (EC= 5 μS cm^{-1}) was added to the flask followed by 4 drops of Ferroin indicator and titrated with 0.5 N $FeSO_4$. As the end point is approached, the solution colour changes from blue-green to reddish-grey. A blank was also run in the same manner without soil to standardize the $K_2Cr_2O_7$. Soil organic carbon content was then calculated using Equation 3.7:

$$Organic\ carbon\ (\%) = \frac{0.003\ g\ \times N \times 10\ mL\ \times \left(1 - \left(\frac{S}{B}\right)\right)}{ODS} \times 100 \qquad \textbf{Equation 3.7}$$

where 0.003 g is the 1N Dichromate solution, which is equivalent to 3 mg of carbon, N is the concentration of $K_2Cr_2O_7$ (1 N), 10 mL is the added volume of $K_2Cr_2O_7$. S and B are the volume of $FeSO_4$ used in sample and blank titration (mL), respectively. ODS is the oven dry soil weight (g).

3.4. Soil physical and mineralogical measurements

3.4.1. Particle size distribution (PSD) analysis.

Particle size distribution was determined using an adaptation of the hydrometer method described by Gee and Bauder (1986). Forty grams of oven-dried soil (<2 mm, oven dried at 65 °C for 24 hours) were measured and placed into 350 mL plastic bottles. If the soil was particularly sandy, up to 80 g was used. 50 mL of 10% sodium hexametaphosphate $(NaPO_3)_6$ (Calgon) and 5 mL of sodium hydroxide (NaOH; 0.6M) were added to the soils. The bottle was then filled with approximately 150 mL of deionised water. Afterwards, the mixture was shaken on an end-over-end shaker at least 24 hours. The suspension was carefully transferred to a 1000 mL measuring cylinder, the leftover soil particles within the 350 mL bottles were washed into the 1000 mL measuring cylinder with deionised water and the cylinders were then made up to 1000 mL. The suspensions were then homogenised using a plunger rod and allowed to stand for the appropriate amount of time before measurement. This entire process was repeated without soil in order to obtain a blank solution to account for the incorporation of sodium hexametaphosphate and sodium hydroxide. Clay and silt were measured at 5 minutes and 27 seconds from the top 10 cm, while the clay was measured after 5 hours. Measurements were taken using a soil hydrometer (ASTM152H, Carlton glass, Australia). Clay, silt and sand percentages were then determined as calculated below.

$$Clay + silt\ (\%) = \frac{S_{5mins} - B_{5mins}}{W_s} \times 100$$ **Equation 3.8**

$$Clay\ (\%) = \frac{S_{5hrs} - B_{5hrs}}{W_s} \times 100$$ **Equation 3.9**

$$Silt\ (\%) = \left(clay + silt\ (\%)\right) - clay\ (\%)$$ **Equation 3.10**

$$Sand\ (\%) = 100 - \ clay + silt\ (\%)$$ **Equation 3.11**

where S and B are soil suspension and blank solution (without soil) hydrometer readings, respectively. W_s refers to soil weight in grams.

3.4.2. X-Ray diffraction analysis of the clay fractions

Clay mineralogy was analysed via X-Ray diffraction (XRD) analysis of the clay fraction (<2 µm), which was separated by sedimentation of dispersed clay in deionised water using Stokes law (Jackson, 2005). No dispersing agents or chemical treatments (such as for organic matter or oxide removal) were added. The collected clay solutions were placed in the oven to dry at 40 °C. Dry clay samples were finely ground and backfilled into steel containers 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. XRD data were collected and displayed 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 using computer-aided search/match algorithms. 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. The semi-quantitative estimation of clay phases for all 10 soils are presented in Figure 3.2, and the Mineralogical composition of clays (%) from X-Ray diffraction analysis listed in Table 3.2.

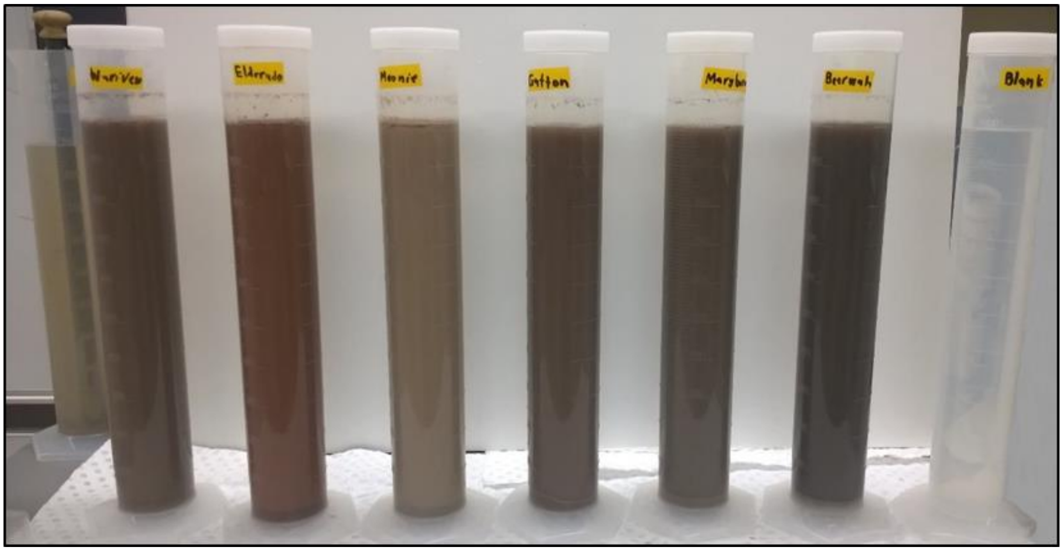

Figure 3.1 Suspensions of selected soils prepared for measurement of particle size distribution using the hydrometer method.

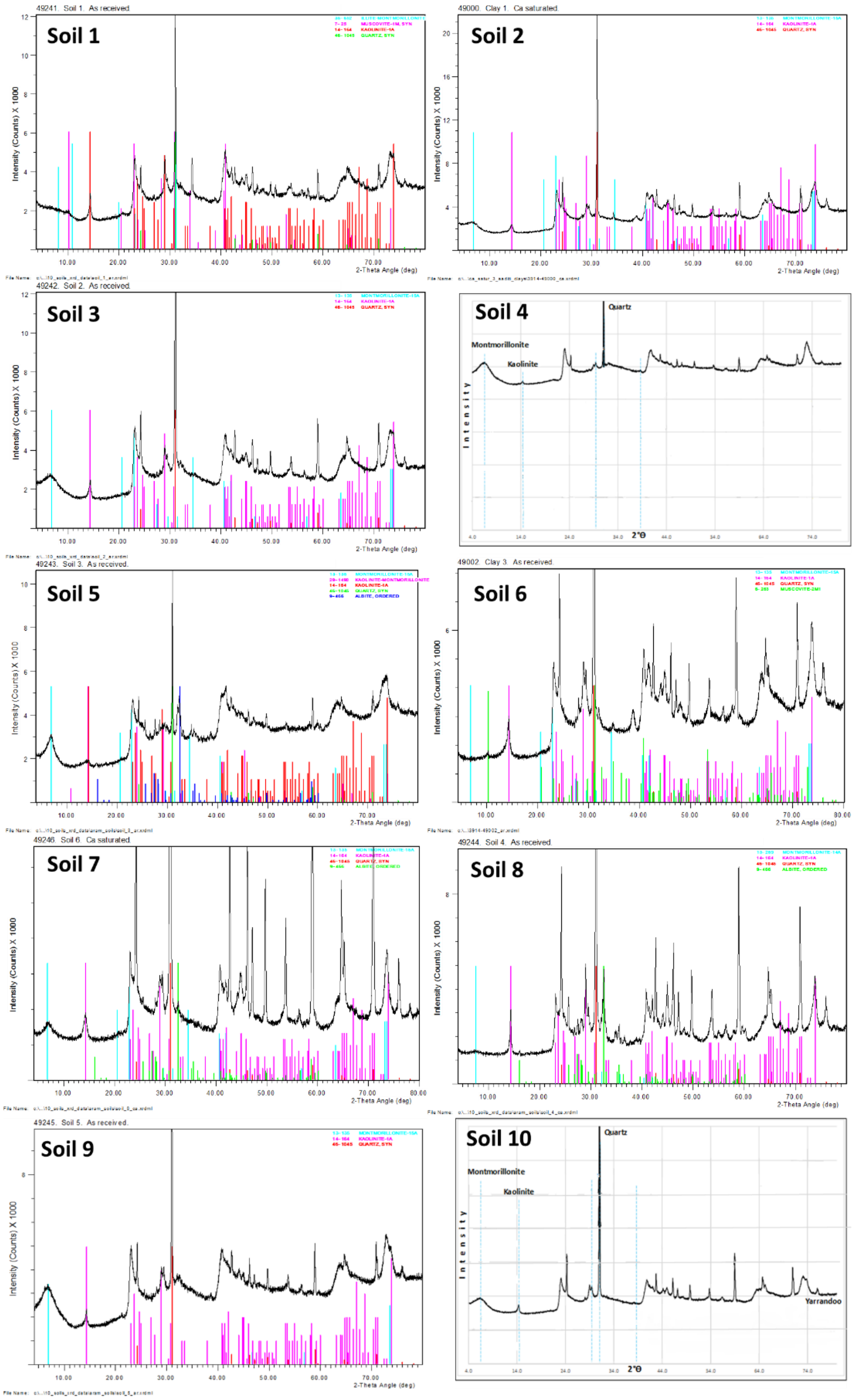

Figure 3.2 X-Ray diffraction (XRD) analysis of the clay fractions of selected soils.

Table 3.2 Mineralogical composition of clays (%) from X-Ray diffraction analysis.

Soil	*Montmorillonite*	*Kaolinite*	*Illite/Mica*	*Albite*	*Quartz*
Wariven	15	30	13	–	42
Eldorado	13	34	-		53
Moonie	30	13	–	–	57
Dalby	60	7	-	-	33
Greenmount	50	15	–	–	35
St George	1	29	7		63
Maryborough	3	35	–	13	49
Gatton	3	15	–	30	52
Beerwah	3	33	–	-	64
Yarrandoo	27	21	-	-	52

3.4.3. Spontaneous and mechanical dispersion

Spontaneous and mechanical dispersion were assessed by a modification of the method described by Rengasamy (2002a) and Marchuk et al. (2013). Samples (20 g) of air-dried soils were placed into 120 mL transparent measuring cylinders and 100 mL of deionised water (EC= 5 µS m^{-1}, pH= 7) was added slowly down the sides of the cylinders, taking care to avoid disturbance of the soil specimen. The soil suspension was allowed to equilibrate overnight. Afterwards, any particles which had dispersed from the soils were gently stirred into suspension and allowed to stand for 4 hours based on Table 3.3. Suspensions were pipetted out from the 50 mm solution depth for turbidity measurements.

For mechanical dispersion assessment, the same process was repeated for the undisturbed soil suspension. After allowing soil suspensions to settle overnight, samples were shaken for 1 hour in an end-over-end shaker (0.5 rev sec^{-1}). After a suitable sedimentation time (Table 3.3), the dispersed clay was pipetted out of the 50 mm solution depth to estimate the dispersed clay. The dispersed clay (<2 µm) particles dispersed from both spontaneous and mechanical processes, was measured using a Hach 2100N Laboratory Turbidimeter at 25°C and recorded in Nephelometric Turbidity Units (NTU). The turbidity of these soils then converted to dispersed clay percentage based on the method of Zhu et al. (2016).

Equation 3.12

$$Clay(\%) = 0.677T\left(\frac{V}{m}\right)d \times 100$$

where 0.677 is the average $\left(\frac{c}{T}\right)$ from particle concentration, c, and turbidity (T). m (mg) and V are the soil mass and water volume (combined as a ratio) of the initial soil-water mixture, and d is the dilution rate of the mixture for turbidity measurement.

Table 3.3 Sedimentation times for particles having an equivalent spherical diameter of 2.0 µm and specific gravity 2.61 falling 50 mm in the water at temperatures between 20 to 30 °C (Rengasamy, 2002a).

Temperature (°C)	**20**	21	22	23	24	25	26	27	28	29	30
Time (hours)	**4**	3.55	3.48	3.43	3.38	3.33	3.28	3.23	3.20	3.15	3.10

3.4.4. Critical flocculation concentration (CFC)

Forty grams of air-dried soil (≤2 mm) were transferred into 350 mL plastic bottles. Approximately 150 mL of deionised water (EC = 5 µS cm^{-1}, pH = 7) was added to the soil, without the addition of any chemical. The mixture was shaken on an end-over-end shaker for at least 24 hours. The suspension was transferred into a 1000 mL measuring cylinder, and the cylinders were then made up to 1000 mL. The <2 µm clay fraction was collected by sedimentation of dispersed clay in deionised water as per Stokes law. This process was repeated until a sufficient amount of soil clay was collected for each soil. The collected clays were saturated with calcium, magnesium, sodium and potassium by washing several times with 1M concentration $CaCl_2$, $MgCl_2.6H_2O$, NaCl and KCl. Clay suspensions were then dialysed against deionised water until external water had an electrical conductivity of 5.0 µS cm^{-1}, based on the method of Rengasamy (1983), and free from chloride. The dialysed clay suspensions were used to determine CFC via a modified method of Rengasamy and Oades (1977). A volume of 30 ml with a concentration of 1 g clay L^{-1} of each dialysed clay was placed into transparent 50 mL Falcon tubes. These were placed on an end-over-end shaker for 10 minutes and then allowed to settle for 6 hours. The concentration of clay in suspension was measured using a Hach 2100N Laboratory Turbidimeter at 25 °C. The range of concentrations of solutions was prepared for CFC determination. The electrolyte concentration that stimulated a 95% flocculation of clay was defined as the CFC (Kaplan et al., 1996). After approximate CFC determination, this test was duplicated using a narrower concentration range to determine a more accurate CFC. The remaining suspension was analysed for turbidity, EC and pH.

The dialysis processes and CFC measurements for each cation and soil are presented in Appendix A, Figure A.1 and Table A.1.

3.4.5. Zeta potential measurement

The electrophoretic mobility and the zeta potential (ζ-potential) of the clay (<2 μm particles) after spontaneous and mechanical dispersion were measured by laser Doppler velocimetry on a Malvern Zeta Master Particle Electrophoresis Analyser, as described in Marchuk and Rengasamy (2011). The correlation functions were measured automatically, and zeta potential was calculated by Malvern Zetasizer family software v7.11. The cell alignment and set up of the system were completed and the operating conditions of the instrument were checked and calibrated using DTS1017 zeta cuvettes at 25 °C prior to testing the samples. The zeta cuvette was calibrated for each lot of samples by Malvern standard solution before each individual run. The zeta cuvette electrodes were wiped with tissue paper and rinsed three times with deionised water before each run. The cuvettes are considered to be disposable, and each cuvette was subjected to no more than 60 ζ-potential measurements. The ζ-potential was calculated as the mean of 15 runs, each of which was averaged of 25 individual measurements performed automatically by the instrument.

Table 3.4 Physical and chemical properties of the soils in this study.

Properties	***Unit***	***Soil***									
		Wariven	***Eldorado***	***Moonie***	***Dalby***	***Greenmount***	***St George***	***Maryborough***	***Gatton***	***Beerwah***	***Yarrandoo***
pH (1:5)		8.9	8.8	8.3	7.2	7.4	7.1	4.5	5.3	5.2	7.4
EC (1:5)	dS m^{-1}	0.34	0.30	0.33	0.21	0.09	0.05	0.08	0.05	0.02	0.21
Total alkalinity	mg L^{-1}	207	157	164	75	89	55	0	15	7	55
SAR	(mmol$_c$ L^{-1})$^{-0.5}$	1.9	4.3	6	3.1	0.2	0.1	0.9	1.9	1.8	0.96
CROSS	(mmol$_c$ L^{-1})$^{-0.5}$	2.5	4.6	6.7	3.5	0.3	0.5	1.2	2.5	2	1.12
ESP	%	3	11.68	9.9	0.2	0.4	0.6	3.2	7.7	8.2	7.89
EDP	%	4.4	12.5	11	1.6	2	2.3	5.2	10	9.2	9.4
CEC	cmol$_c$ kg^{-1}	13.9	15.4	30.6	64.7	46.9	7.6	2	1.8	5.8	23.2
Organic carbon	%	1.1	1.6	0.6	1.3	1.6	1.6	1.5	1.6	1.3	1.01
Chloride (Cl^-)	mg kg^{-1}	174	60	8	120	30	20	33	10	10	55
Nitrate (NO_3-N)	mg L^{-1}	18	60	1200	17	0.1	0.7	1	0.6	0.1	24.5
CFC of (Mg)§		0.63	0.71	0.73	0.73	0.58	0.49	0.62	0.71	0.66	0.73
Clay	%	28.8	33.8	46.3	62.3	30.3	12.5	15.0	10.0	9.5	52.1
Silt	%	12.8	16.3	6.3	15.8	13.8	5.0	22.5	10.0	4.8	14.8
Sand	%	58.5	50.0	47.5	21.9	56.0	82.5	62.5	80.0	85.8	33.1
Spontaneous ζ-potential	-mV	24.8	34.4	29.1	23	24.7	32	29.2	29.7	28.9	16
Mechanical ζ-potential	-mV	25.3	37.8	28.3	25	25.4	35.2	32.8	35.1	32.8	18.2
Australian taxonomic class		Brown Dermosol	Red Dermosol	Grey Vertosol	Black Vertosol	Brown Vertosol	Red Kandosol	Grey Kurosol	Yellow Chromosol	Grey Chromosol	Black Vertosol
USDA soil taxonomic class		Inceptisol	Inceptisol	Vertisol	Vertisol	Vertisol	Inceptisol	Ultisol	Alfisol	Alfisol	Vertisol

§the equivalent effectiveness of flocculation power of magnesium relative to calcium. EC is electrical conductivity; SAR is sodium adsorption ratio; CROSS is cation ratio of soil structural stability; ESP is exchangeable sodium percentage; EDP *is* exchangeable dispersive percentage; CEC is cation exchange capacity and ζ-potential is zeta potential.

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4. Effect of irrigation water pH on saturated hydraulic conductivity and electrokinetic properties of acidic, neutral and alkaline soils

Abstract

The demand for the use of marginal quality water as an irrigation resource is increasing in arid and semi-arid region lands due to the freshwater shortage. Marginal waters usually have high salinity, high alkalinity and may contain high proportions of ions such as sodium. This study investigated the impact of irrigation water pH on the saturated hydraulic conductivity (K_s), cation exchange capacity, net particle charge and dispersivity of soils. Nine soils with differing pH, alkalinity, clay content and mineralogy were used in leaching column experiments with solutions of varying sodium adsorption ratio (20 and 40), electrical conductivity (0.8, 1.5, 2.5, 5, 10, 25 and 50 dS m^{-1}) and pH (6, 7, 8 and 9). The desired pH was achieved by adjusting the HCO_3^-/Cl^- ratio and carbon dioxide partial pressure using CO_2 gas with 99.9% purity. Results showed that the increase of solution pH causes an increase in net negative charges on clay particles, resulting in higher exchangeable cations, negative zeta potential, and clay dispersion and movement of dislodged particles into pore spaces, resulting in K_s reduction. This effect was more evident for acidic and low clay content soils. The K_s reduction in relation to pH was less for smectitic and high clay content soil than for kaolinite dominant soils for all concentrations, suggesting resiliency of the smectitic soils under irrigation water with high pH. Results reinforce that it is essential to consider the original pH, clay content and mineral of the soil and the pH, EC and SAR of the irrigation water to accurately predict the K_s reduction of the soil.

Keywords: hydraulic conductivity reduction, alkalinity, soil pH, clay content, clay dispersion, zeta potential.

4.1. Introduction

Globally, marginal quality water usage for irrigation is increasingly becoming a common practice, due to the scarcity of fresh water in arid and semi-arid regions (Ezlit et al., 2013; Murtaza et al., 2006). Marginal waters may be sourced directly from aquifers [such as coal seam gas (CSG) water] or from effluent/waste sources (Bennett & Warren, 2015) following the use of either groundwater or surface water. Such waters may be marginal in quality for a variety of reasons – for example elevated salinity, very low or very high pH, or high sodicity (Bennett et al., 2016a; Kinnon et al., 2010; Taulis & Milke, 2013). Subsequently, the use of marginal quality water can increase the potential for soil structural degradation and permeability reduction (Bennett et al., 2019a); for example, excess sodium contributed by the water can result in both intra- and inter-crystalline swelling leading to eventual dispersion (Dang et al., 2018a; Ezlit et al., 2013). This effect can be enhanced or reduced depending on the electrical conductivity (EC) of the irrigation water (Dang et al., 2018d; Schofield, 1947).

Current evaluations of the effect of marginal quality water on soil structure focus mainly on the concentration of Na and cationic composition, expressed via parameters such as sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP). The effects of SAR and EC on K_s have been reported widely with high SAR of waters and low EC causing clay swelling and dispersion, reducing K_s (McNeal & Coleman, 1966; Quirk & Schofield, 1955; Shainberg et al., 1981). Additionally, potassium is known to have a variable effect of soil structural decline (Dang et al., 2018c; Farahani et al., 2019; Marchuk & Marchuk, 2018; Zaker & Emami, 2019; Zhu et al., 2019b), whilst magnesium has been shown to increase disaggregation but not result in dispersion (Zhu et al., 2019b; Zhu et al., 2019a). These effects are soil specific and depend on the soil clay content and mineralogy, soil organic matter and the electrolyte composition and concentration (Menezes et al., 2014; Shainberg & Letey, 1984; Shainberg & Singer, 1990).

Suarez et al. (1984) showed that the pH in combination with SAR and EC resulted in a further decrease in K_s, where this decrease was greater than the effect of SAR and EC alone. Analytical studies to examine the specific effects of pH (as an independent variable) on soil flocculation-dispersion behaviour considered changes in net charge on clay particles (Bolan et al., 1996; Chorom & Rengasamy, 1995; Chorom et al., 1994; Goldberg & Glaubig, 1987; Marchuk et al., 2013). These studies identified that the net negative charge of clay particles is a primary factor affecting instability of soil structure, at a given pH and ionic strength, further dependent on the organic matter content and clay mineral suite in the soil. In the case of variable charge soils, structural stability and flocculation are expected to occur at the pH value corresponding to the point of zero charge (PZC), where net charge is zero (Rengasamy et al., 2016; Sposito, 2008). Deviation in pH from the PZC causes an increase in net charge, resulting in disaggregation, dispersion and hydraulic reduction. This phenomenon leads to permanent (without significant mechanical intervention) reduction in soil infiltration capacity and water availability, which in the field, can lead to increased surface runoff, flooding and soil erosion (Rengasamy, 2002a; Viviani & Iovino, 2004). Suarez and Rubio (2010) stated that even a small increase in the pH can be associated with a reduction in the infiltration rate and hydraulic conductivity of soils. However, the effects of solution pH on the K_s of soils across a range of pH, alkalinity and clay mineralogy are less well understood.

Soils normally have pH ranging from 4 to 10 (Szabolcs, 1989) and the pH in a specific soil is a result of the soil clay minerals, organic matter, associated ion exchange and hydrolysis reactions (Sumner et al., 1991). Subsequently, the pH can vary substantially down a soil profile. Arid and semi-arid region soils are often alkaline in the subsoil with high ESP (Bronick & Lal, 2005; Quirk & Schofield, 1955; Suarez et al., 1984). Mashhady and Rowell (1978) indicated that the main factors responsible for alkaline pH are partial CO_2 pressure and concentration of CO_3^{-2} and HCO_3^- ions in the cracking clay soils (Vertosols), subsoils of Ultisols, Alfisols and Calcisol soils. Non-alkaline soils may also have high ESP in acidic conditions (pH<6) in humid environments (El-Swaify, 1973; Rengasamy, 2010). El-Swaify (1973) revealed that K_s is affected by anion concentration in some tropical soils–mainly due to different pHs. Globally, the majority of studies associated with the effect of pH on soil physicochemical properties have occurred on a narrow range of soils in terms of initial pH condition, geographic location and clay content, with limited soil classification variation, especially in Australian soils. In Australia, the effect of changing pH on the dispersion of clay soils was mainly investigated in relation to changes in net negative charge and clay particles (Chorom, 1996; Chorom et al., 1994; Marchuk et al., 2013; Rengasamy & Olsson, 1991). Thus, further investigations are necessary to examine the influences of the pH of marginal quality waters on soil aggregate stability and the K_s of a wider range of Australian soils.

The aim of this study was therefore to investigate the impact of different pH solutions on K_s reduction, net negative charge and the exchangeable cations for Australian soils of varying soil pH and clay content. The potential role of pH was investigated under two SAR regimes at SAR of 20 and 40 with sequentially decreasing EC in order to evaluate the magnitude of pH, EC and SAR effects on K_s reduction dynamics, consistent with the work of Suarez et al. (1984).

4.2. Material and methods

4.2.1. Soil selection and initial characterisation

Nine soils were collected from 0–30 cm depth from Queensland and New South Wales states in Australia (Table 4.1). The soils were selected in order to span a range of properties such as pH and alkalinity, clay content, and mineralogy. The soils were air dried and crushed with sufficient energy to breakdown the aggregates to pass through a 2-mm sieve; care was taken to not apply energy greater than required in order to maintain the physical bonds of the aggregates <2 mm. The electrical conductivity (Method 3A1), pH (Method 4A1), soluble and exchangeable cations (Method 15A2) measured using standard methods of Rayment and Lyons (2011), total alkalinity quantified by reaction with hydrochloric acid (HCl, 0.1M) in a titration method using a Radiometer analytical titration instrument (TIM845, Titration Manager), soil particle size distribution determined by the hydrometer method (Gee & Bauder, 1986), and organic carbon (Walkley & Black, 1934) are presented in Table 4.1.

The SAR, cation ratio of soil structural stability (CROSS), exchangeable dispersive percentage (EDP), and ESP were calculated after measurement of soluble and exchangeable cations of the original samples (Table 4.1).

The concept of CROSS [Equation 4.1, (Rengasamy & Marchuk, 2011)] was proposed to replace SAR due to the differential flocculation powers of Mg and Ca and the differential dispersive effects of Na and K on soils (Rengasamy & Marchuk, 2011). The EDP suggested by Bennett et al. (2016a) as a new index to replace ESP and it was calculated because of the major contribution of Mg in solution composition in this study. However, a recent study conducted by Zhu et al. (2019b) confirmed that the dispersive coefficient of [Mg] has a negligible effect on the soil structural stability and can be removed from EDP equation and suggested redefining the equation in the same manner that (Bennett et al., 2016a) had expressed it. Therefore, the EDP was determined as a function of cations within the solid phase in dispersive soils (Equation 4.2).

Table 4.1 Physical and chemical properties of selected soils.

Properties	***Soil***								
	1	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***
pH (1:5)	8.9	8.8	8.3	7.2	7.4	7.1	4.5	5.3	5.2
EC (1:5)	0.34	0.30	0.33	0.21	0.09	0.05	0.08	0.05	0.02
Total alkalinity	207	157	164	75	89	55	0	16	7
SAR	1.9	4.3	6.0	3.1	0.2	0.1	0.9	1.9	1.8
CROSS	2.5	4.6	6.7	3.5	0.3	0.5	1.2	2.5	2
ESP	3.0	11.7	9.9	0.2	0.4	0.6	3.2	7.7	8.2
EDP	4.4	12.5	11	1.6	2	2.3	5.2	10	9.2
EPP	5.2	4.7	2.9	2.4	1.3	10.7	3.1	14.3	2.4
CEC	13.9	15.4	30.6	64.7	46.9	7.6	2.0	1.8	5.8
Organic carbon	1.1	1.6	0.6	1.3	1.6	1.6	1.5	1.6	1.3
Chloride (Cl^-)	174	60	8	120	30	20	33	10	10
Nitrate (NO_3-N)	18	60	1200	17	0.1	0.7	1.0	0.6	0.1
CFC of (Mg)§	0.63	0.71	0.73	0.73	0.58	0.49	0.62	0.71	0.66
Clay	29	34	46	62	30	13	15	10	10
Silt	13	16	6	16	14	5	23	10	4.8
Sand	59	50	48	22	56	83	63	80	86
Australian taxonomic class	Brown Dermosol	Red Dermosol	Grey Vertosol	Black Vertosol	Brown Vertosol	Red Kandosol	Grey Kurosol	Yellow Chromosol	Grey Chromosol
USDA soil taxonomic class	Inceptisol	Inceptisol	Vertisol	Vertisol	Vertisol	Inceptisol	Ultisol	Alfisol	Alfisol
Location in Australia	28°58'29"S, 150°26'38"E Yallaroi, NSW	28°54'50.48"S, 150°16'18.6"E North Star, NSW	27°49'50"S, 150°9'13.9"E Moonie, QLD	27°13'48"S, 151°19'12"E Dalby, QLD	27°48'32.8"S, 151°54'22.2"E Greenmount, QLD	27°58'8.4"S, 148°22'51.6"E St. George, QLD	25°21'36"S, 152°44'40.44"E Maryborough, QLD	27°35'44.9"S, 152°18'20.1"E Gatton, QLD	26°51'19.3"S, 152°59'23.46"E Beerwah, QLD

§the equivalent effectiveness of flocculation power of magnesium relative to calcium. EC is electrical conductivity in dS m^{-1}; total alkalinity in mg L^{-1}; SAR is sodium adsorption ratio in ($mmol_c$ L^{-1})$^{-0.5}$; CROSS is cation ratio of soil structural stability in ($mmol_c$ L^{-1})$^{-0.5}$; ESP is exchangeable sodium percentage; EDP is exchangeable dispersive percentage; EPP is exchangeable potassium percentage, CEC is cation exchange capacity in $cmol_c$ kg^{-1}; organic carbon in mg kg^{-1}; chloride in mg kg^{-1}; Nitrate in mg L^{-1}; clay, silt and sand are in percentage.

$$CROSS = \frac{[Na] + 0.56[K]}{\sqrt{\frac{[Ca] + 0.6[Mg]}{2}}}$$

Equation 4.1

$$EDP\% = \frac{[Na] + 0.556[K]}{CEC} \times 100$$

Equation 4.2

where Na, K, Ca and Mg in Equation 4.1 are concentration of these cations in soil solution (mmol$_c$ L^{-1}) while Na and K in Equation 4.2 are their concentrations in exchangeable sites (cmol$_c$ kg^{-1}). The CEC is calculated as the sum of the exchangeable cations.

Clay mineralogy was determined by X-Ray diffraction (XRD) analysis of the clay fractions using a PANalytical X'Pert Pro Multi-purpose diffractometer. The XRD patterns for randomly oriented air-dried samples were recorded with XRD data were collected and displayed 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. Specific clay mineral identification criteria were based on Brown and Brindley (1980) and Moore and Reynolds (1989). The detailed procedure for clay mineralogy determination using XRD is described in Dang et al. (2018b).The semi-quantitative estimation of clay phases for all 9 soils are presented in Table 4.2.

Table 4.2 Mineralogical composition of clays (%) from X-Ray diffraction analysis.

Soils	*Montmorillonite*	*Kaolinite*	*Illite/Mica*	*Albite*	*Quartz*
1	15	30	13	–	42
2	13	34	–	–	53
3	30	13	–	–	57
4	60	7	–	–	33
5	50	15	–	–	35
6	1	29	7		63
7	3	35	–	13	49
8	3	15	–	30	52
9	3	33	–	–	64

4.2.2. Solution preparation

An ion mixed concentration approach was used to obtain the desired level of solutions by mixing $NaHCO_3$, $MgCl_2$. $6H_2O$ and NaCl chemical compounds. Mixtures of Na and Mg salts rather than Na and Ca salts were used to prepare the solutions at each pH to prevent $CaCO_3$ precipitation at high pH and low SAR. The Mg concentration was calculated based on the soil specific flocculation power relative to calcium from a critical flocculation concentration (CFC) experiment (it is explained further on in the text) (Table 4.1). The solutions were prepared to form SAR 20 and SAR 40, with salinity of 0.8, 1.5, 2.5, 5, 10, 25 and 50 dS m^{-1} and pH of 6, 7, 8 and 9 [these values were chosen to be consistent with the work of Suarez et al. (1984)]. The effective SAR (SAR_{eff}) values were calculated based on the effective flocculation power of Mg (Equation 4.3)

$$SAR_{eff} = \frac{Na}{\sqrt{\frac{XMg}{2}}} \qquad \textbf{Equation 4.3}$$

where X is the effective flocculation power of Mg shown for each soil in Table 4.1 (Na and Mg are concentrations in $mmol_c\ L^{-1}$), SAR_{eff} is expressed in $(mmol_c\ L^{-1})^{-0.5}$

The desired pH was achieved by adjusting the HCO_3^-/Cl^- ratio and carbon dioxide partial pressure (P_{CO2}) to within ±0.05 units of the desired pH, where the pH 9 and 6 solutions were the same except that the pH 9 solutions were equilibrated at atmospheric CO_2 ($P_{CO2} \approx 35Pa$) and the pH 6 solution at $P_{CO2} \approx 97$ kPa using CO_2 gas with 99.9% purity following the method of Suarez et al. (1984). This approach was used rather than the addition of other alkali or acidic compounds for pH adjustment to avoid the change in ionic composition and electrolyte concentration of solutions. The pH 6 solutions were achieved by bubbling CO_2 gas into the 5 L solution container. The pH of the solution was measured in the solution container before degassing could occur.

4.2.3. Hydraulic conductivity experiment design

0.3 kg soil samples were carefully packed into polyvinyl chloride (PVC) cylinders (87.5 mm inner-diameter), with mesh bottoms for drainage, to attain a mean bulk density of 1.4 g cm^{-3}. The soil columns were saturated by capillary tension from the bottom upwards using the same solution applied to measure hydraulic conductivity. A constant head of 20 mm was maintained in the measurement of hydraulic conductivity. Each soil column was initially leached with the most concentrated solution of the desired pH and SAR treatments. When the K_s of the soil columns and pH of the effluent had stabilised, the next more diluted solution of the same SAR and pH was applied. A steep osmotic gradient between the soil solution and the surface of soil aggregates potentially induces sudden aggregate breakdown (osmotic explosion) (Shainberg et al., 1981). To avoid the opportunity for the osmotic explosion phenomenon, the electrolyte concentration was reduced gradually in this study. Three replicates for each treatment and soil were used to determine K_s, creating a total of 216 soil cores for all soils used in this study.

The constant-head, saturated hydraulic conductivity (K_s) method (Klute, 1965) was used by measuring the volumes drained at different time intervals (t) using Darcy's law formula (Equation 4.4), where V is the volume of solution (cm^3), L is the length of the soil core (cm), A is the cross-sectional area of the soil column (cm^2) and H is the water head extending from the top of the ponded solution to the depth of the soil core (cm). Steady state was determined after no less than 7 pore volumes had passed the core, which was sufficient for solute breakthrough and equilibration to occur. The units for K_s, are cm s^{-1} in this study.

$$K_s = \frac{VL}{AHt}$$ **Equation 4.4**

The changes in hydraulic conductivity between treatments were represented as a relative hydraulic conductivity (r_{Ks}; Equation 4.5) for comparison purposes, the K_s values were compared to the initial K_s ($K_{s\,(i)}$) values determined with the 10 dS m^{-1}, SAR 20 solution, or 50 dS m^{-1}, SAR 40 solution.

$$r_{K_s} = \frac{K_{s(i,n)}}{K_{s(i)}}$$ **Equation 4.5**

At the conclusion of the experiment, the columns were air-dried and the top 1 cm of soil columns was used for zeta potential (ζ-potential) and spontaneous dispersion (turbidity) measurement using the lowest electrolyte concentration (0.8 dS m^{-1}) at each desired pH, based on a procedure of Marchuk et al. (2013). The turbidity of these soils then converted to dispersed clay percentage based on the method of Zhu et al. (2016).

4.2.4. Zeta potential measurement

The electrophoretic mobility and the zeta potential (ζ-potential) of the clay (<2 μm particles) after spontaneous dispersion were measured by laser Doppler velocimetry on a Malvern Zeta Master

Particle Electrophoresis Analyser, as described in Marchuk and Rengasamy (2011). The correlation functions were measured automatically and zeta potential calculated by Malvern Zetasizer family software v7.11. The cell alignment and set up of the system were completed and the operating conditions of the instrument were checked and calibrated using DTS1017 zeta cuvettes at 25 ºC prior to testing the samples. The zeta cuvette electrodes were wiped with tissue paper and rinsed three times with deionised water before each run. The ζ-potential were calculated as the mean of 15 runs, each of which was averaged from 25 individual measurements performed automatically by the instrument.

4.2.5. Critical flocculation concentration (CFC)

The <2µm fractions of the clays were collected by sedimentation of dispersed clay in deionised water using Stokes law. The collected clays were saturated with calcium and magnesium by washing several times with 1M concentration $CaCl_2$, $MgCl_2.6H_2O$. Clay suspensions were then dialysed against deionised water until external water had an electrical conductivity of 5 µS cm^{-1}, based on the method of Rengasamy (1983), and free from chloride. The dialysed clay suspensions were used to determine CFC via a modified method of Rengasamy and Oades (1977). 30ml at 1 g L^{-1} of each dialysed clay was placed in transparent 50 mL Falcon tubes, placed on an end-over-end shaker for 10 minutes and then allowed to settle for 6hrs. The concentration of clay in suspensions was measured using a Hach 2100N Laboratory Turbidimeter at 25ºC. The range of concentrations of solutions were prepared for CFC determination. The electrolyte concentration that stimulated a 95% flocculation of the clay was defined as the CFC (Kaplan et al., 1996). After approximate CFC determination, this test was duplicated using a narrower concentration range to determine more accurate CFC. The remaining suspension was analysed for turbidity, EC and pH.

4.2.6. Exchangeable cations and exchangeable dispersive potential (EDP)

Another experiment was conducted to investigate the effects of solution pH on the exchangeable cations. The exchangeable cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) of the treated soils were determined by modified methods of Rayment and Lyons (2011). Soil samples (8 g) were equilibrated twice with 40 mL of SAR 20 solution of 50 dS m^{-1} (pH adjusted) and then equilibrated three times with pH 6, 7, 8 and 9 solutions at different solute concentrations. Exchangeable cations were determined using 0.5M NH_4Cl and pH adjusted, as described in Rayment and Lyons (2011) and the extracts were analysed by inductively coupled plasma atomic mass spectroscopy (Perkin Elmer Nexion ICP-MS). The cation exchange capacity (CEC) and EDP were calculated after measurement of exchangeable cations from treated soils.

4.2.7. Statistical Analysis

Significant differences between K_s results for different EC and pH treatments were first determined by one-way ANOVA with interactions at the 95% confidence interval ($\alpha = 0.05$) unless otherwise mentioned. Differences between K_s where ANOVA returned significant results were observed by performing Tukey's honest significant difference analysis.

4.3. Results

4.3.1. Effect of pH on hydraulic conductivity

The saturated hydraulic conductivity (K_s) of each soil, for each of the pH and EC combinations at SAR 20 and 40, are presented as relative hydraulic conductivity (r_{Ks}) in Figure 4.1 and Figure 4.2. The K_s is clearly affected by increasing pH, with this effect more evident for acidic soils, particularly in solutions lower than 5 dS m^{-1}. The onset decrease in r_{Ks} was observed at a lower salinity for smectitic soils — observed as dispersed clay evident in the collected leachates — with swelling of clays increasing the standing height of the soil column (accounted for within the K_s calculation). The pH dependence of K_s reduction for the montmorillonite dominant clays was less than kaolinite dominant soils for all concentrations and sodium levels.

The initial soil pH was apparently important in terms of the mechanisms driving hydraulic decline. That is, as the initial pH approached alkaline conditions, the effect of pH for a given EC and SAR becomes less pronounced. There is a general trend that the higher pH treatment solution results in lower r_{Ks}, although there is no significant difference within these initially alkaline soils for that trend. The exception to this for initially alkaline soils is where the SAR of the solution was 40, and/or at very low electrolyte concentration. These results support the fact that as the initial pH approaches alkaline conditions, the solution EC and SAR become more important in driving hydraulic decline than the pH.

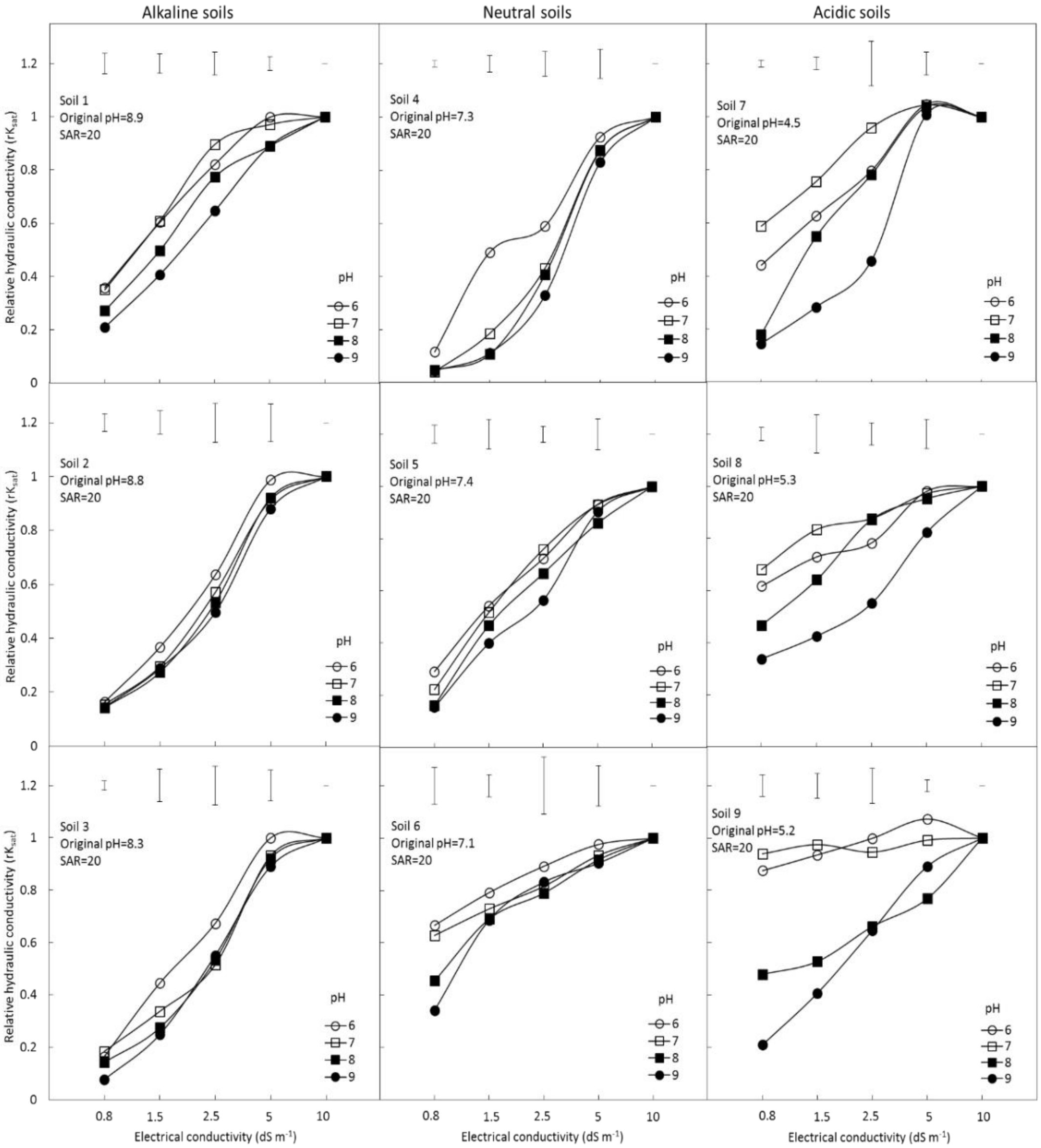

Figure 4.1 Relationship between relative hydraulic conductivity (r_{Ks}) and electrolyte concentration for soils at SAR=20 and pH of 6, 7, 8 and 9. Bars represent Tukey's honest significant difference (±HSD) values for each EC.

In general, the greatest difference in r_{Ks} was achieved for acidic soils at treatment pH>7. Indeed, where the pH of the treatment solutions had a significant effect, this was usually at pH 8 or pH 9, irrespective of initial soil pH. The magnitude of reduction in K_s was the primary difference between initially acidic and alkaline soils. pH 9 instigated the highest K_s reduction for all soils in particular at low electrolyte concentration levels. Higher reductions in K_s occurred at SAR 40 than at SAR 20 (Figure 4.1 and Figure 4.2), as might be expected given the breadth of research into sodicity and its effects.

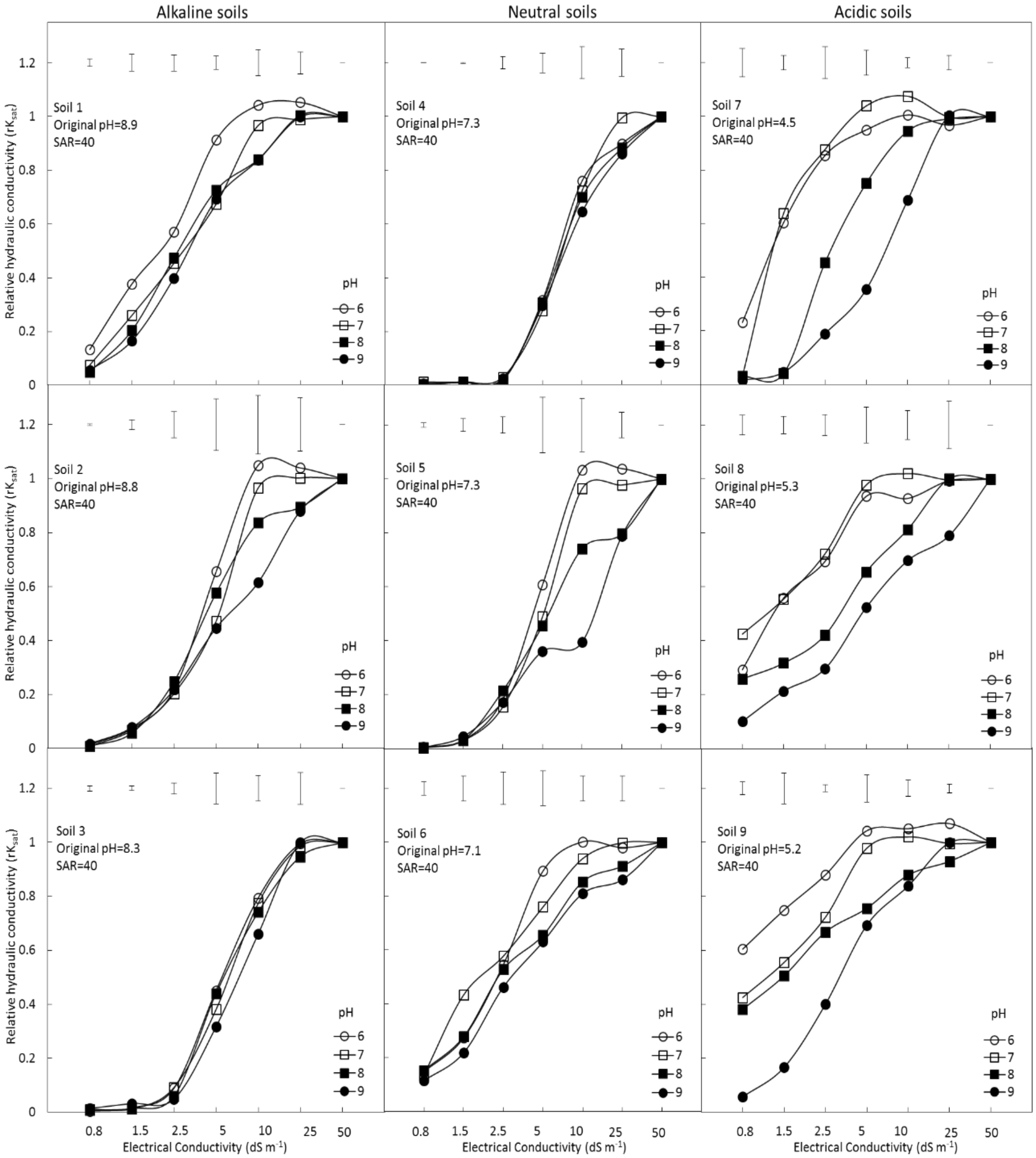

Figure 4.2 Relationship between relative hydraulic conductivity (r_{Ks}) and electrolytes concentration for soils at SAR=40 and pH of 6, 7, 8 and 9. Bars represent Tukey's honest significant difference (±HSD) values for each EC.

For some of the soils, a slight increase occurred in r_{Ks} initially with lower subsequent electrolyte concentration. This may have been due to the development of air bubbles entrapped in packed soil columns during initial capillary wetting to measure K_s (Suarez et al., 1984), change in solution viscosity (Olsen, 1960), or reformation of pore networks (considered to be less likely). The result was considered to have a negligible effect on the experimental outcomes.

4.3.2. Clay content and hydraulic conductivity reduction

The greatest K_s reduction occurred in soils with high clay contents (Figure 4.3) and is especially noticeable for the high montmorillonite clay content soils, but is ubiquitous in terms of occurrence as pH and SAR increases, while EC decreases (Figure 4.1 and Figure 4.2). Figure 4.3 considers the soil environment when the electrolyte osmotic effect is largely eased, demonstrating that the degree of reduction in K_s increases with increasing clay content, consistent with a power function. Regressions for the aggregated data demonstrate very strong fit between clay content and hydraulic reduction of R^2=0.79 and 0.84 for the SAR 20 and 40 soil solutions, respectively. Considering the data at each individual pH for a given SAR improved the regression fit substantially (Table 4.3).

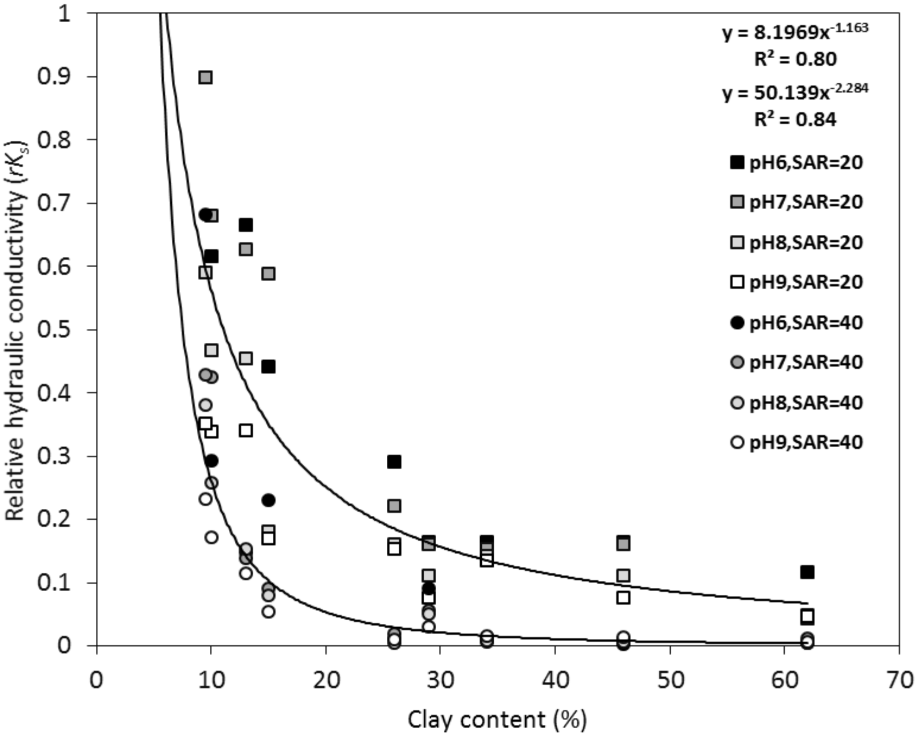

Figure 4.3 Correlation plots for hydraulic conductivity reduction with respect to clay content for solutions with pH of 6, 7, 8 and 9 and sodium adsorption ratio 20 and 40 at electrolyte concentration 0.8 dS m^{-1}.

Table 4.3 Regression equations between reduction in hydraulic conductivity (y) and clay content (x) for the individual pH treatments, at the respective sodium adsorption ratio (SAR), plotted in Figure 4.3. The electrolyte concentration of the solution was 0.8 dS m^{-1}. R^2 is Pearson's correlation coefficient and RMSE is root mean square error.

SAR	*pH*			
	6	**7**	**8**	**9**
20	$y=8.46x^{-1.068}$ $R^2=0.93$ RMSE=0.076	$y=22.17x^{-1.416}$ $R^2=0.93$ RMSE=0.073	$y=6.62x^{-1.144}$ $R^2=0.90$ RMSE=0.062	$y=3.63x^{-1.026}$ $R^2=0.89$ RMSE=0.038
40	$y=250.5x^{-2.764}$ $R^2=0.87$ RMSE=0.089	$y=40.05x^{-2.148}$ $R^2=0.86$ RMSE=0.062	$y=61.39x^{-2.404}$ $R^2=0.84$ RMSE=0.039	$y=10.26x^{-1.819}$ $R^2=0.88$ RMSE=0.024

4.3.3. Effect of pH on dispersivity and net particle charge

Changes in exchangeable cations and EDP as influenced by the pH of solutions are shown for SAR 20 in Table 4.4. The effects of pH on clay dispersion and ζ-potential of soils, after sequentially lower electrolyte concentration solutions were applied, at the respective constant pH, for each r_{Ks} measurement are also presented in Table 4.5. In general, where the treatment solution pH increased, subsequently increasing the soil pH, there was a concomitant increase in the CEC, EDP and dispersive behaviour of aggregates, as well as an increase in the ζ-potential negativity. These effects were more evident for low clay content and acidic soils than clay and alkaline soils, although the change for pH 6 to pH 9 was significant for all soils and all factors.

Table 4.4 Cation exchange capacity (CEC (cmol$_c$ kg^{-1}) and exchangeable dispersion percentage (EDP) as a function of pH. Values are averaged from 0.8, 1.5, 2.5, 5 and 10 dS m^{-1} with SAR of 20. Differing lower-case letters within a specific soil indicate significant changes due to pH of solutions; significance is determined at p<0.05.

Soils	*pH6*		*pH7*		*pH8*		*pH9*	
	CEC	*EDP%*	*CEC*	*EDP%*	*CEC*	*EDP%*	*CEC*	*EDP%*
1	24.4ab	10.1a	24.2a	9.6a	24.8b	18.7b	25.4b	20.7c
2	22.4a	11.8a	21.9a	11.3a	23.2a	20.2b	26.8b	21.1b
3	26.4ab	11.1a	27.0b	10.3a	26.5a	19.5b	28.7b	22.6c
4	44.5a	12.0a	50.4b	11.1a	50.9b	18.3b	53.5c	19.3b
5	34.4a	11.2a	35.1abc	10.8a	36.2b	18.9b	40.0c	19.5b
6	6.2a	17.1a	6.4a	16.3a	6.9ab	25.4b	7.8b	23.2c
7	4.0a	23.3a	4.2abc	21.0b	6.2b	31.4c	7.1c	32.3c
8	3.3a	27.2a	3.9ab	25.6a	5.1b	43.7b	7.0c	41.6c
9	4.9a	17.3a	5.4ab	17.0a	6.3bc	30.1b	7.0c	32.2c

All soils exhibited some pH dependence in terms of CEC. The CEC of alkaline, neutral pH and acidic soils increased by approximately 10%, 20% and 75%, respectively, for the change in pH from 6 to 9 (Table 4.4).

4.4. Discussion

4.4.1. Controlling mechanisms of hydraulic reduction

The results showed that an increase in pH results in higher K_s reduction in soils regardless of clay content, mineralogy, organic carbon and original pH at different ionic concentration and SAR of 20 and 40. The difference in K_s reduction occurred as result of the extent of the increase in exchangeable cations, exchangeable sodium and precipitation of Ca^{2+} and Mg^{2+} cations at higher pH values and dispersive potential (Table 4.4). This pronounced effect has been attributed to the increase in net negative charge of clay particles for high pH values (Chorom & Rengasamy, 1995; Chorom et al., 1994), which is thought to be a primary factor for instability of soil structure, at a given pH and ionic strength. These results support findings where pH>8, with a source of sodium applied, resulted in an increase in the soil solution SAR due to calcium and magnesium precipitating (Mashhady & Rowell, 1978; Suarez et al., 1984). This phenomenon is expected to cause a vast reduction in permeability (McNeal & Coleman, 1966), resulting from clay swelling, disaggregation and dispersion, leading to geometric reduction of pore size and pore blockage (Rengasamy & Marchuk, 2011; Shainberg et al., 1981). However, the degree of this degradative effect depends on the initial properties of soils such as acidity and alkalinity and clay content.

The results indicate that as soils become alkaline and increase in clay content, the effect of EC and SAR dominates the magnitude of hydraulic reduction. Bennett et al. (2019a) and Rengasamy and Olsson (1991) argue that the soil pH will influence the extent of disaggregation to evaluate K_s, which is identified as threshold electrolyte concentration (C_{TH}) to induce dispersion of soils prior to the C_{TH} by affecting the net negative charge; particularly in soils having variable charge clay minerals. However, the increase in pH from 6 through to 9 resulted in significant unstable conditions for all soils, both in terms of EDP and electrophoretic mobility of the soil clays. These factors are responsible for causing soil structural degradation and subsequently lowering K_s; which is further consistent with earlier results of Suarez et al. (1984). They found that pH resulted in greater K_s reduction for their soils at equivalent EC and SAR values.

Table 4.5 The dispersed clay and zeta potential (ζ) for soils at the end of the experiment after sequential solutions applied of SAR 20 and 40 and pH of 6,7,8 and 9.the lowest electrolyte solution (0.8 dS m^{-1}) was used for each pH and SAR. Differing lower-case letters within a specific soil indicate significant changes due to the pH of solutions; significance is determined at $p < 0.05$.

Soils	SAR 20							
	pH6		*pH7*		*pH8*		*pH9*	
	Dispersed clay %	*ζ (-mV)*	*Dispersed clay %*	*ζ (-mV)*	*Dispersed clay %*	*ζ (-mV)*	*Dispersed clay %*	*ζ (-mV)*
1	0.47a	-24.6a	0.61b	-24.4b	0.68c	-25.1c	0.73d	-27.3d
2	0.87a	-26.4a	1.63b	-26.9a	1.64b	-27.4b	1.62b	-27.6b
3	0.07a	-25.9a	0.15b	-25.9a	0.18c	-26.5a	0.29d	-28.4b
4	0.26a	-25.4a	1.78b	-28.0b	2.37c	-27.8b	5.73d	-28.2b
5	0.66a	-25.6a	1.07b	-25.1a	1.08bc	-26.1a	1.15d	-28.1b
6	1.98a	-28.9a	4.01b	-29.8a	4.10b	-29.8a	4.18b	-32.3b
7	6.30a	-34.1a	6.48b	-34.6ab	6.57b	-35.3b	6.82c	-36.1c
8	2.46a	-32.6a	2.43a	-34.0b	2.75b	-34.3bc	3.18c	-36.2d
9	1.37a	-27.2a	1.68b	-27.6a	1.89bc	-31.2b	2.03d	-33.9c
	SAR40							
Soils	*pH6*		*pH7*		*pH8*		*pH9*	
	Dispersed clay %	*ζ (-mV)*	*Dispersed clay %*	*ζ (-mV)*	*Dispersed clay %*	*ζ (-mV)*	*Dispersed clay %*	*ζ (-mV)*
1	0.89a	-29.0a	0.96b	-29.0ab	1.13c	-29.1ab	1.71d	-33.3c
2	3.15a	-31.6a	3.78b	-32.5b	3.98bc	-32.5bc	7.17d	-33.3d
3	0.76a	-32.8a	0.84b	-32.8a	1.30c	-33.7b	1.99d	-37.7c
4	7.21a	-36.2a	8.04b	-36.3a	9.59c	-36.6b	9.95c	-37.6c
5	2.41a	-31.5a	2.90b	-32.8b	3.18c	-34.9c	8.12d	-37.6d
6	5.34a	-35.8a	5.85b	-35.9a	6.36c	-36.6b	6.65d	-38.8c
7	9.55a	-38.9a	9.64a	-37.2b	10.47b	-37.3bc	10.67b	-40.5d
8	2.83a	-38.3a	2.70a	-38.5a	3.33b	-39.3b	3.31b	-41.7c
9	3.82a	-32.2a	4.42b	-32.3a	5.0c	-35.3b	5.28d	-38.7c

The degradative effect of high pH on the tested soils was also believed to be influenced by the clay mineralogy and iron and aluminium oxide compounds (common for acidic soils), although was not statistically tested. It is postulated that these factors allow variation in K_s reduction which is likely due to net negative charge (Murray & Quirk, 1990; Pashley & Quirk, 1989) and ionic composition on the diffuse double layer (DDL) (Sumner et al., 1991), depending on mineralogy and oxide contents (Goldberg, 1989), organic matter dissolution (Goldberg et al., 1990; McDowell, 2003) as well as clay platelet specific surface area characteristics (Van Olphen, 1977).

In the acid soils (and sometimes the neutral soils), the response of K_s reduction at pH 6 and 7 tended to cluster closer together, with heightened K_s reduction approaching pH 8 and, in particular, pH 9. The significant difference in K_s reduction within acidic soils for the different pH solution equilibrium resulted from high exchangeable sodium, removing Ca^{2+} and Mg^{2+} from the system, and presumably the amount of variable charge within the clay mineral suite —inferred from the change in net negative charge with pH (Table 4.4 and Table 4.5). Acidic soils dominated by variable surface charge clays are typically strongly weathered and contain clay minerals such as kaolinite (McKenzie et al., 2004). Another reason for the greater K_s reduction within initially acidic soils, with variation in solution pH equilibrium, might be due to the reduction of aluminium and iron oxides at high pH (e.g. pH 8 and 9), as described by Goldberg (1989). Finally, in the low CEC soils (Soils 6–9) the exchangeable potassium was >10% of the CEC for two of the soils, which may be suggested to have effect in terms of enhancing the tendency to disperse (Dang et al., 2018c; Farahani et al., 2019), although sufficient volumes of solution were percolated to facilitate chemical solution breakthrough and equilibration, meaning it is suggested that a potassium effect could not explain the differences. Therefore, it is suggested that the degradative effect on K_s was from a combination of factors affecting the net negative charge of the soils and was enhanced by the removal of iron oxides. On this basis, and the work of Goldberg (1989) iron oxide removal is hypothesised as the primary reason for the greater magnitude of declining aggregate stability and K_s reduction in the initially acidic soils.

The effects of altering pH were less visible for higher clay content, and alkaline soils, in comparison to acidic and lower clay content soils. This was most likely as a result of the tendency of clay soils to swell (dominated montmorillonite clay mineral), and the differential amount of dispersed clay required to block pores within smaller pore geometry (clay soils) as opposed to larger pore geometry (sandy soils) for all examined pH values. The low clay content, sandy soils would require a greater proportion of the total clay volume to disperse in order to cause a percent reduction in K_s equivalent to disaggregation properties in high clay content soils (Bennett et al., 2019a; Ezlit et al., 2013). These findings suggest that future work needs to further investigate acidic and high clay content soils against a range of alkaline and low clay content soils to complement this data set. However, Figure 4.3 demonstrates rather definitely that clay content is a reasonable indicator of the sensitivity for alterations in hydraulic conductivity anticipated for soils treated with different pH of the applied solution.

4.4.2. The role of pH in modelling hydraulic decline

In the modelling of r_{Ks}, pH has typically been treated as an independent factor (e.g. HYDRUS; Šimůnek et al., 2016) and our results suggest that this potentially ascribes too much systematic control to pH, especially in systems with an initially alkaline pH. The initial alkalinity of a soil is found to be an important consideration in the extent of hydraulic reduction for different solution pHs. Alkaline soils were less prone to large percent reduction in hydraulic conductivity with changing solution pH, but were still responsive. The acidic soils demonstrated high susceptibility for K_s reduction when increasing the pH, which cannot be separated from the clay content effect. Our results demonstrate that the clay content can be used as a primary criterion to predict the effect of pH within a soil swelling, disaggregation and dispersion model. Bennett et al. (2019a) confirm that clay content is a crucial variable in determining the extent of hydraulic reduction, and subsequently the resilience of soil structure stability. Therefore, future work needs to focus on the establishment of a refined pH modelling algorithm accounting for the magnitude effect of soil pH and the clay content of soils within an EC and SAR solution system.

4.4.3. Practical implications

The results of this study suggest that understanding the extent of adverse effects of pH in combination with EC and SAR is essential for appropriate soil management and practical use of marginal quality irrigation water. The soils exhibited different degrees of susceptibility to the deleterious effects of pH and increasing EDP, enhancing dispersivity with increasing alkalinity. A similar trend was observed in the study of Gupta et al. (1984) for the increase of alkalinity and sodium concentration in irrigation water. However, common to all soils, the direct use of irrigation water with pH>8, such as untreated coal seam gas (CSG) water (Bennett et al., 2016b), or many other sources of groundwater and industry wastewater (Biggs & Binns, 2015), cannot be suitable for irrigation purposes without appropriate treatment. Suarez et al. (1984) argue that high sodium concentration in soil is normally associated with high pH ($pH \geq 8$), due to the precipitation of Ca^{2+} and Mg^{2+} in irrigated lands, as a result of high pH and sodic irrigation water application. The degree of reduction in K_s at 0.8 and 1.5 dS m^{-1} (common values for most irrigation waters in Australia) increases with increasing clay content, particularly evident in alkaline soils and neutral soils, and this is more pronounced at SAR 40 where there is strong persistence of the reduction evident. The implication being that the more clayey the soil, the more salt is required to maintain, or improve [e.g. Ali et al. (2018)], soil structure stability. However, simply increasing the electrolyte concentration of a solution to maintain soil structure is not advisable where salts are stored in the root-zone without a leaching fraction (Shaw & Thorburn, 1985) and/or where the percolating solution electrolyte concentration exceeds plant growth thresholds. In terms of practical agriculture, this suggests that a balance between the solution electrolyte concentration and reduction of solution alkalinity is a more suitable approach.

While the deleterious effects of high pH can be minimised through buffering the soil system with an electrolyte source, such as gypsum (Ali et al., 2018), or other soluble Ca^{2+} sources, to offset sodium in the system (Menezes et al., 2014), this is inefficient where the alkalinity is not first addressed, leading to excessive electrolyte application to maintain soil stability. The K_s reduction observed for the different pH, EC and SAR in this work suggest that caution is needed to avoid disaggregation with added solution alkalinity. The implication is the need to maintain an irrigation solution pH below 8 from a management perspective. This can be through irrigation water treatment and soil treatments using acid-forming materials (e.g. gypsum, sulphur and or sulphuric acid) (Bennett et al., 2016b; McKenna et al., 2019). Currently there is little consideration given to irrigation solution alkalinity and addressing this prior to irrigation occurring. Additionally, where the irrigation water alkalinity is considered, this usually results in the irrigation water being discarded as a potential resource, as treatment is not normally considered. Our work demonstrates that while soils had a somewhat specific response to irrigation solution alkalinity, there was a general and overriding trend that could facilitate simple guidelines for treatment regimes using existing geochemical software such as PHREEQC (Parkhurst & Appelo, 2013). However, to predict K_s reduction of the soil accurately, it is essential to consider the clay content, original pH of the soil, as well as the pH, EC and SAR of the irrigation water. In this sense, this means that the lower limit of treatment will vary with these factors, and some water may not need treatment at all for a specific soil. Determining these lower limits for treatment and safe application of saline-sodic and alkaline waters will determine the economic feasibility of using the water without undue environmental harm, and in some cases realise a strategic irrigation resource that is not currently being utilised. It would be pertinent to ensure that such information is supplied and required for monitoring within irrigation guidelines, such as the ANZECC (2000) guidelines used in Australia and New Zealand.

4.5. Conclusion

The results of this study clearly reinforce that pH influences soil K_s reduction and clay dispersion via altering the net negative charge on the surface of clay particles. Importantly, the soil K_s is largely dependent on the original pH of the soil, in particular for acidic soils and kaolinitic soils, while alkaline and smectitic soils were less susceptible to increasing pH. In high clay content, alkaline and neutral soils, the disaggregation, dispersion and swelling mechanisms were largely controlled by the EC and SAR of the equilibrium solution. The pH was observed to either cause a significant reduction in these soils, or have a consistent trend of reduction, although the magnitude of the pH effect was overridden by the magnitude of the EC and SAR dynamic effects. For the lower clay content and acidic soils, increasing pH had a vast effect on the hydraulic decline, indicating that the mechanisms for hydraulic reduction shift depending on the initial conditions of the system.

Increased equilibrium solution pH caused an increase in net negative charges on clay particles and resulted in increased CEC, dispersivity and negative ζ-potential for all soils. These effects were more noticeable for pH 9 solutions, and in acidic soils, with increased net negative charge apparently a major reason for clay dispersion and hydraulic reduction.

This work suggests that to accurately predict the K_s of the soil it is essential to consider the clay minerals, initial soil system conditions and the pH, EC and SAR of the irrigation water.

4.6. References

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5. A pH based pedotransfer function for scaling saturated hydraulic conductivity reduction: Improved estimation of hydraulic dynamics in HYDRUS

Abstract

Hydraulic conductivity is a key soil property governing agricultural production and is thus an important parameter in hydrologic modelling. The pH scaling factor for saturated hydraulic conductivity (K_s) reduction in the HYDRUS model was reviewed and evaluated for its ability to simulate K_s reduction. A limitation of the model is the generalisation of K_s reduction at various levels of electrolyte concentration for different soil types; i.e. it is not soil-specific. In this study a new generalised linear regression model was developed to estimate K_s reduction of a larger set of Australian soils, in comparison to three American soils. A nonlinear pedotransfer function was also produced using the Levenberg–Marquardt optimisation algorithm, by considering pH and electrolyte concentration of the applied solution, as well as the soil clay content. This approach improved the estimation of the pH scaling factor relating to K_s reduction for individual soils. The functions were based on K_s reduction of nine contrasting Australian soils using two sets of treatment solutions of sodium adsorption ratio of 20 and 40, with total electrolyte concentration of 8, 15, 25, 50, 100, 250 and 500 mmol$_c$ L^{-1} and pH of 6, 7, 8 and 9. The comparison of the experimental data and model outputs indicates that the models performed objectively well and successfully described K_s reduction due to the pH. It was further emphasised that a nonlinear function provided greater accuracy compared to the generalised function, for the individual soils of Australia and California. This indicates that the nonlinear model provides an improved estimation of the pH scaling factor for K_s reduction of specific soils in the HYDRUS model, and should therefore be considered in future HYDRUS developments and applications.

Keywords: solution pH, hydraulic conductivity, pedotransfer function, modelling, scaling factor, HYDRUS.

5.1. Introduction

Soil hydraulic conductivity is a critically important soil physical property used in determining water-solute transport, infiltration rate, groundwater recharge and other agricultural and hydrological processes (Ben-Hur et al., 2009); Smith et al. (1995). Soil hydraulic conductivity is strongly dependent on soil structural status and stability, and the geometry of pore spaces in the soil (Assouline & Narkis, 2011). The use of marginal quality irrigation water is likely to cause: deterioration in soil structure; change in the ratio of solids, water and air within the soil; and reduced hydraulic conductivity, due to clay disaggregation and dispersion processes (Bennett et al., 2019a; Quirk & Schofield, 1955; Rengasamy & Olsson, 1991). Reduction in hydraulic conductivity often occurs as a result of excess sodium within the soil solution (measured as the sodium adsorption ratio, SAR), which can result in both intra- and inter-crystalline swelling leading to clay dispersion (Dang et al., 2018a; Ezlit et al., 2013). The magnitude of the reduction in hydraulic conductivity depends on the electrolyte concentration (EC) in the soil solution (Quirk & Schofield, 1955; Shainberg & Letey, 1984). Furthermore, Suarez et al. (1984) showed that the pH of the solute percolating a soil, in combination with high SAR and low EC, was likely to lead to decreased hydraulic conductivity beyond the combined SAR and EC effect alone. The effects of pH, EC and SAR of an applied solution on soil hydraulic conductivity have been broadly investigated, experimentally and mathematically, using predictive models (Chorom et al., 1994; Ezlit et al., 2013; McNeal & Coleman, 1966; Suarez & Rubio, 2010).

Predictive models have become efficient tools to investigate water flow and solute movement in soils under irrigation. Performance of multiple simulations considering various equilibrium and kinetic non-equilibrium chemical reactions between major ions allows industry and research to quickly interrogate the dynamics of systems. However, the development of models for the prediction of soil structural degradation and hydraulic conductivity dynamics will only be as good as the functions and assumptions that underlie them. Modelling saturated hydraulic conductivity reduction remains a challenging task, due to the combined effect of sodicity, salinity, pH and alkalinity, within the context of soil being an inherently heterogeneous and complex material that is non-rigid (Campbell & Paustian, 2015; Miller & White, 1998). Therefore, the effect of a given solution chemistry can lead to unique soil structural dynamics within soils of different origin (Bennett et al., 2019a; Bennett & Warren, 2015; Menezes et al., 2014; Quirk & Schofield, 1955), soil clay content and mineral suite (Bell, 1996; Goldberg & Glaubig, 1987), soil organic matter (Oades, 1984), the pH of soil solution (Bolan et al., 1996; Suarez et al., 1984), and the ionicity of the soil aggregate system (Bennett et al., 2019a; Marchuk & Rengasamy, 2012; Zhu et al., 2019b). Moreover, the magnitude and the interrelationship of these factors provide variable levels of resilience of soils to structural degradation for a given intervention. Therefore, soil hydraulic dynamics should not be expected to be simply predicted with a generalised model.

The HYDRUS model is perhaps the most widely utilised soil hydraulic model (Šimůnek et al., 2016). The empirical and semi-empirical equations for the adverse effects of SAR, EC, and pH of solutions are described within the HYDRUS program manual (Šimůnek et al., 2013). McNeal (1968) used a semi-empirical equation based on the experimental clay swelling function for montmorillonite clay treated with combined sodic and saline solutions to fit experimental curves related to the relative saturated hydraulic conductivity (K_s). The effect of solution pH on the K_s is derived from Suarez et al. (1984), whereby the change in K_s is characterised by a negative effect of pH on soil hydraulic conductivity, independent of EC and SAR, which is explained by an additional scaling factor. Suarez et al. (1984) investigated the effects of pH on K_s of three soils of California in the United States of America, for a combination of solution SAR and EC concentrations; i.e. pH cannot be thought of as completely independent of the SAR and EC, as this is not physically possible. The results of the Suarez et al. (1984) study, using a narrow range of soils, have become the main dataset for the prediction of K_s reduction due to the pH of the applied solution. Furthermore, this dataset was subsequently used to produce a linear function (Equation 5.4) to simulate r_{Ks} reduction due to pH in the UNSATCHEM and HYDRUS mathematical models of Suarez and Šimůnek (1997) and Šimůnek and Suarez (1997).

The use of this reduction model is likely to provide less accurate prediction of K_s for different soils (Šimůnek & Suarez, 1997), but to some extent helps to identify the degree of K_s reduction due to pH of applied solutions. Therefore, there is a global need to optimize and validate the model parameters for pH induced K_s reduction within the HYDRUS model, and more broadly for use as a pedotransfer function. However, the approaches to validate and calibrate the models vary depending on the complexity involved in parameterising of models. Šimunek et al. (2012) indicated that model calibration and inverse parameter estimation can be carried out using a relatively simple, gradient based, local optimisation approach based on the Marquardt-Levenberg method, which is directly implemented into the HYDRUS codes; and it is also important that the estimated model is both efficient and robust. This paper reviews the HYDRUS model for K_s reduction due to pH of the applied solution and suggests modifications to the current reduction model and its parameters. This is achieved by combining Levenberg-Marquardt nonlinear parameter optimisation involving EC and pH of the applied solution, as well as the soil clay content, to improve the accuracy of modelled solute and water movement, on a soil-specific basis.

5.2. Review of theoretical background

Within HYDRUS, the hydraulic conductivity K is calculated by multiplying a scaling factor r with the initial saturated hydraulic conductivity K_s and the relative hydraulic conductivity K_r. The scaling factor r is a function of the soil solution pH, SAR and EC and K_r is a function of the hydraulic pressure head:

$$K(h, pH, SAR, EC) = r(pH, SAR, EC)\, K_S \;\; K_r(h)$$

Equation 5.1

Here, K is the hydraulic conductivity (cm d^{-1}), h is the pressure head (cm), pH is the solution pH (-Log[H^{+}]), SAR is the sodium adsorption ratio, EC is the total electrolyte concentration of the solution in mmol$_c$ L^{-1}, and r is a scaling factor (function of pH, SAR and EC). Subsequently, the scaling parameter, r, in Equation 5.2 is divided into two sub factors:

$$r(pH, SAR, EC) = r_1(SAR, EC)\, r_2(pH)$$

Equation 5.2

where r_1 is a function of SAR and EC, providing the disaggregation (inter- and intra-crystalline swelling) and dispersion effects on the hydraulic conductivity, as described by Quirk and Schofield (1955), Dang et al. (2018a), and Bennett et al. (2019a). Additionally, r_2 represents the effects of solution pH on the hydraulic conductivity (Suarez et al., 1984). The assumption is that the scaling parameters r_1 and r_2 can be applied for the entire range of pressure heads under unsaturated conditions. Where the values of r_1 and r_2 equate to 1.0, the soil chemistry supports the maximum hydraulic conductivity.

The scaling parameter r_1 is based on the clay-swelling model of McNeal (1968). This describes the reduction of K_s in terms of exchangeable sodium percentage (ESP) and electrolyte concentration using a montmorillonite interlayer swelling factor. The relationship between r_1 and the clay-swelling model (x) is calculated by McNeal (1968) and can be written as:

$$r_1 = 1 - \frac{cx^n}{1 + cx^n}$$ **Equation 5.3**

where c and n are empirical parameters for a given soil within a specified range of soil ESP, and x is the clay-swelling model calculated by McNeal (1968) based on the adjusted ESP and solution concentration. While beyond the scope of this paper, it is noted here that the McNeal (1968) model was modified by Ezlit et al. (2013) to function on a soil-specific basis via a semi empirical disaggregation approach. Dang et al. (2018d) validated the specificity and the disaggregation model for field soils, while Bennett et al. (2019a) demonstrated the magnitude of soil variability, even for the same soil orders. Therefore, in seeking to improve the soil-water dynamics of HYDRUS, it is prudent to utilise the semi-empirical approach of Ezlit et al. (2013), as well as seek to improve the incorporation of pH effects.

The r_2 scaling factor, for the effect of pH on the hydraulic conductivity was calculated from experimental data of Suarez et al. (1984) after first seeking to correct K_s reduction for the adverse effects of low electrolyte concentration and high exchangeable sodium using r_1 (Equation 5.3); an attempt to provide the pH effect as independent to the SAR and EC combined effects. The following equation was developed by Suarez and Šimůnek (1997) and Šimůnek and Suarez (1997) based on the negative effects of pH of the applied solution from the study of Suarez et al. (1984):

$$r_2(pH) = \begin{cases} 1.0, & \text{for } pH \leq 6.83 \\ 3.46 - 0.36pH, & \text{for } 6.83 < pH < 9.3 \\ 0.1, & \text{for } pH \geq 9.3 \end{cases}$$ **Equation 5.4**

The upper and lower pH limits are an assumption of no change in K_s or near complete reduction for the specified pH ranges. In the text below, we will refer to this model as the HYDRUS K-pH-dependent function. Consequently, the final hydraulic conductivity reduction, due to pH, SAR and EC of the applied solution, is calculated (Šimůnek & Suarez, 1997):

$$K(h, pH, SAR, EC) = r(pH, SAR, EC)\, K_S\, K_r(h) = r_1(SAR, EC) r_2(pH)\, K_S\, K_r(h) \quad \textbf{Equation 5.5}$$

Equation 5.5 assumes that r_1 and r_2 have an equivalent weighted effect on the hydraulic reduction of the system, which allows the pH scaling factor to assert a large amount of control on the hydraulic system that may not necessarily be warranted.

5.3. Materials and methods

5.3.1. Soil selection and initial characterisation

Nine soils were collected from the 0–30 cm depth of soils located in Queensland and New South Wales states, Australia (Table 5.1). The selection of these soils was based on their difference in initial pH and alkalinity, as the primary selection factor. A secondary selection factor was the soil clay mineralogy and texture. The soils were air dried and crushed with sufficient energy to breakdown the aggregates to pass through a 2-mm sieve; care was taken to not apply energy greater than required in order to maintain the physical bonds of the aggregates <2 mm. Using standard methods from Rayment and Lyons (2011), the electrical conductivity (Method 3A1), pH (Method 4A1), soluble and exchangeable cations (Method 15A2) were measured. The alkalinity was determined using a Radiometer Analytical Titrator (TIM845, Titration Manager). Particle size distribution was measured by the hydrometer method (Gee & Bauder, 1986), clay mineralogy by X-ray diffraction (Jackson, 2005) and organic carbon (Walkley & Black, 1934). The soil characteristics are presented in Table 5.1.

5.3.2. Solution preparation

The desired levels of pH, EC and SAR of the experimental treatment solutions were obtained by mixing $NaHCO_3$, NaCl and $MgCl_2.6H_2O$ chemical compounds. Mixtures of Na and Mg salts rather than Na and Ca salts were used to prepare the solutions at each pH to prevent $CaCO_3$ precipitation at high pH and low SAR. The Mg concentration was calculated based on the soil specific flocculation power from cation flocculation concentration (CFC) experiments relative to calcium (Table 5.1), based on the modified method of Rengasamy and Oades (1977).

Table 5.1 Properties of the soils used (0–30 cm depth).

Properties	***Soil***								
	1	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***
pH (1:5)	8.9	8.8	8.3	7.3	7.4	7.1	4.5	5.3	5.2
EC (1:5)	34	30	33	19	9	5	8	5	2
Total alkalinity	207.2	157.1	164.3	75.0	89.3	55.0	0.0	15.7	7.0
SAR	1.9	4.3	6.0	3.1	0.2	0.1	0.9	1.9	1.8
CROSS	2.5	4.6	6.7	3.5	0.3	0.5	1.2	2.5	2.0
ESP	3.0	11.68	9.9	0.2	0.4	0.6	3.2	7.7	8.2
EDP	4.4	12.5	11	1.6	2	2.3	5.2	10	9.2
CEC	13.9	15.4	30.6	64.7	46.9	7.6	2.0	1.8	5.8
Organic carbon	1.1	1.6	0.6	1.3	1.6	1.6	1.5	1.6	1.3
Chloride (Cl^-)	174.0	60.0	8.0	120.0	30.0	20.0	33.0	10.0	10.0
Nitrate (NO_3-N)	18.0	60.0	1200.0	17.0	0.1	0.7	1.0	0.6	0.1
CFC of (Mg)[§]	0.63	0.71	0.73	0.73	0.58	0.49	0.62	0.71	0.66
Clay	28.8	33.8	46.3	62.3	30.3	12.5	15.0	10.0	9.5
Silt	12.8	16.3	6.3	15.8	13.8	5.0	22.5	10.0	4.8
Sand	58.5	50.0	47.5	21.9	56.0	82.5	62.5	80.0	85.8
Australian taxonomic class	Brown Dermosol	Red Dermosol	Grey Vertosol	Black Vertosol	Brown Vertosol	Red Kandosol	Grey Kurosol	Yellow Chromosol	Grey Chromosol
USDA soil taxonomic class	Inceptisol	Inceptisol	Vertisol	Vertisol	Vertisol	Inceptisol	Ultisol	Alfisol	Alfisol
Location in Australia	28°58'29"S, 150°26'38"E Wariven, NSW	28°54'50.48"S, 150°16'18.6"E Eldorado, NSW	27°49'50"S, 150°9'13.9"E Moonie, QLD	27°13'48"S, 151°19'12"E Dalby, QLD	27°48'32.8"S, 151°54'22.2"E Greenmount, QLD	27°58'8.4"S, 148°22'51.6"E St. George, QLD	25°21'36"S, 152°44'40.44"E Maryborough, QLD	27°35'44.9"S, 152°18'20.1"E Gatton, QLD	26°51'19.3"S, 152°59'23.46"E Beerwah, QLD

[§] the equivalent effectiveness of flocculation power of magnesium relative to calcium. EC is electrolyte concentration in $\text{mmol}_c\ L^{-1}$; total alkalinity in mg L^{-1}; SAR is sodium adsorption ration in $(\text{mmol}_c\ L^{-1})^{-0.5}$; CROSS is cation ratio of soil structural stability in $(\text{mmol}_c\ L^{-1})^{-0.5}$; ESP is exchangeable sodium percentage; EDP is exchangeable dispersive percentage; CEC is cation exchange capacity in $\text{mmol}_c\ 100g^{-1}$; organic carbon in percentage; chloride in mg kg^{-1}; Nitrate in mg L^{-1}; clay, silt and sand are in percentage.

The leaching solutions, SAR 20 and 40 were prepared at total electrolyte concentrations of 8, 15, 25, 50 and 100 $\text{mmol}_c\ L^{-1}$ for SAR=20 and, 8, 15, 25, 50, 100, 250 and 500 $\text{mmol}_c\ L^{-1}$ for SAR=40 solutions. Both the SAR 20 and 40 solutions were then prepared at an equilibrated pH of 6, 7, 8 and 9, according to the methodology of Suarez et al. (1984). The effective SAR (SAR_{eff}) values were calculated based on the effective flocculation power of Mg (Equation 5.6)

$$SAR_{eff} = \frac{Na}{\sqrt{\frac{XMg}{2}}}$$ **Equation 5.6**

where X is the effective flocculation power of Mg exhibited for each soil (Table 5.1), Na and Mg are concentrations in mmol$_c$ L^{-1}.

The desired pH was achieved by adjusting the $HCO_3^-/C1^-$ ratio and carbon dioxide partial pressure (P_{CO2}) to ±0.05 units of the desired pH; the pH 9 and 6 solutions were the same except that the pH 9 solutions were equilibrated at atmospheric CO_2 (P_{CO2}≈35Pa) and the pH 6 solution at Pco_2≈97 kPa using CO_2 gas with 99.9% purity. This was consistent with the methodology of Suarez et al. (1984) to allow direct comparison with their results. This approach was used, rather than addition of other alkali or acidic compounds, for pH adjustment to avoid the change in ionic composition and electrolyte concentration of solutions. The pH 6 solutions were achieved by continuously bubbling CO_2 gas into the 5.0 L solution container. The pH of the solution was measured in the solution container before degassing could occur.

5.3.3. Preparation for, and measurement of, saturated hydraulic conductivity

An aliquot (300 g) of each soil was carefully packed into polyvinyl chloride (PVC) columns (87.5 mm inner-diameter) – mesh bottoms and a fast filter paper were used to allow drainage – to attain the mean bulk density (1.4 g cm^{-3}) for the nine soils. In a disturbed soil column, the bulk density is somewhat arbitrary, hence the mean value was considered an appropriate selection. The soil columns were initially saturated with the appropriate solution by capillary tension from the bottom of the core. Subsequently, the same solution was applied to the top of the column to measure hydraulic conductivity at a constant hydraulic head of 2.0 cm, in accordance with (Klute, 1965). Leaching commenced with the most concentrated solution of the desired pH and SAR (Figure 5.1). When the K_s of the soil columns, and pH of the effluent had stabilised, the sequentially lower concentration solution of the same SAR and pH was applied. This process was continued until the culmination of the final solution in the sequence.

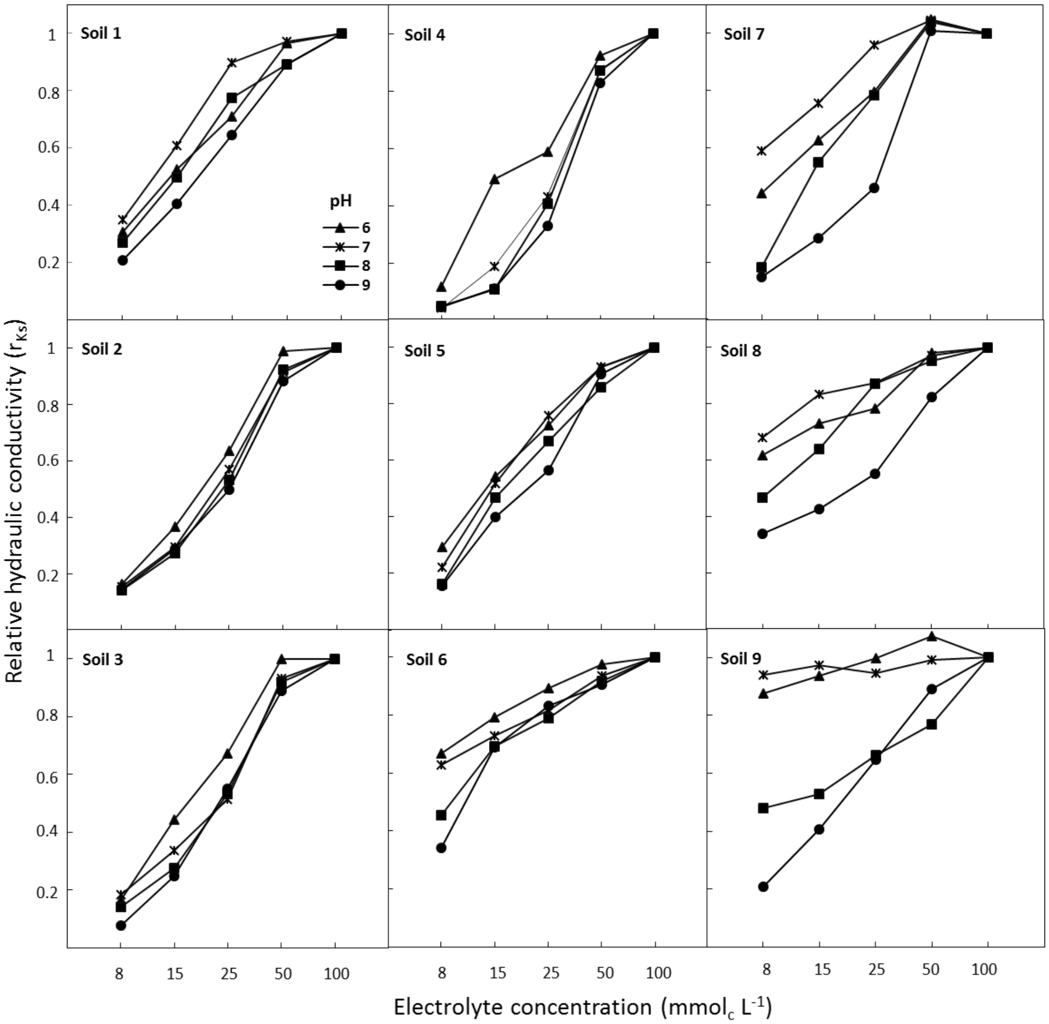

Figure 5.1 Relative hydraulic conductivity (r_{Ks}) versus electrolyte concentration for soils at SAR=20, and pH of 6, 7, 8 and 9.

The leachate solutions were collected from each column in time intervals to calculate K_s using Darcy's Law (Equation 5.7). For the purposes of comparison, the K_s values were compared to the initial K_s values (Equation 5.8) determined as the K_s occurring with the greatest electrolyte concentration (for SAR = 20, the greatest EC was 100 mmol$_c$ L^{-1}, and for SAR = 40 it was 500 mmol$_c$ L^{-1}). The K_s was calculated at sequential time intervals (t) using Darcy's law:

$$K_s = \frac{VL}{AHt}$$ **Equation 5.7**

where V is the volume of solution (cm^3), L is the length of the soil core (cm), A is the cross-sectional area of the soil column (cm^2) and H is the water head extending from the top of the ponded solution to the bottom of the soil core (cm). Three replicates for each treatment and soil were used to determine K_s, creating a total of 216 soil cores for all soils used in this study.

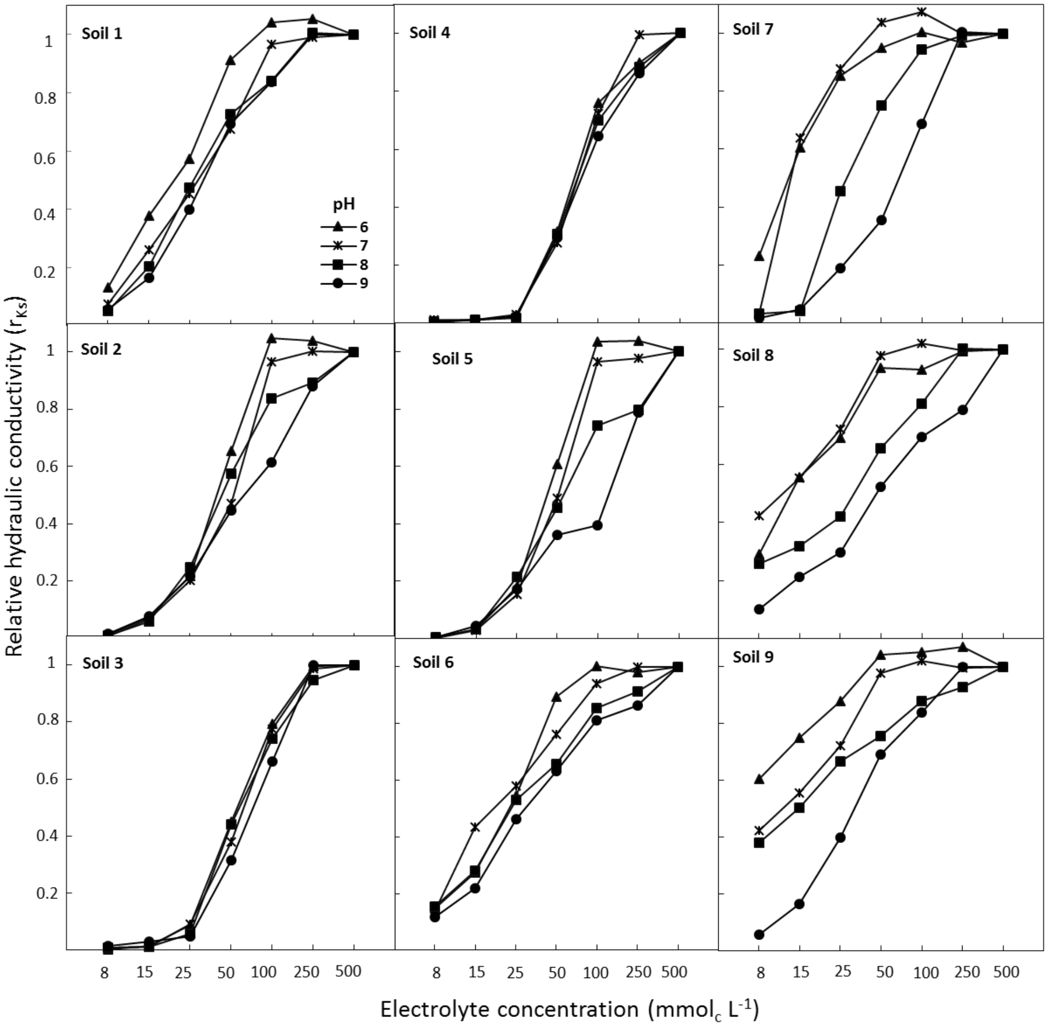

Figure 5.2 Relative hydraulic conductivity (r_{Ks}) versus electrolyte concentration for soils at SAR=40, and pH of 6, 7, 8 and 9.

The changes in hydraulic conductivity between treatments were represented as a relative hydraulic conductivity (r_{Ks}):

$$r_{Ks} = \frac{K_{s_{(i+n_j)}}}{K_{s_i}}$$ **Equation 5.8**

Here, the initial K_s, denoted by i, was compared with the $i+n_j$ sequential K_s to provide a hydraulic conductivity reduction from the initial K_s, where n_j is the j^{th} sequential solution in the sequence of n solutions.

5.4. Modification of the hydraulic reduction scaling factor for pH

5.4.1. Generalised equation

An inverse empirical model for the prediction of the K_s reduction scaling factor, due to the adverse effects of irrigation water pH, was developed from the observed r_{Ks} data (Figure 5.1 and Figure 5.2). The r_2 scaling factor in the HYDRUS proposed by Šimůnek and Suarez (1997) (Equation 5.4) was re-calculated using the experimental r_{Ks} values from the study of Suarez et al. (1984). Subsequently, these r_{Ks} values were compared to the r_{Ks} values for the current experimental results observed at pH 6 ($r_{Ks(pH6)}$) for each EC value, and SAR of 20 and 40. This provided an initial determination of the relative scaling factor (r_{SF}; Equation 5.9) for comparison purposes:

$$r_{SF} = \frac{rK_{s(i,n_i)}}{rK_{s(i)}}$$ **Equation 5.9**

where r_{SF} is the r_{Ks} reduction ratio in comparison to r_{Ks} of pH = 6 ($r_{Ks(i)}$), and n_j is the sequential solution pH in the solution sequence. After calculating the parameters from Equation 5.9, a new r_2 pH scaling factor was then calculated using a linear regression analysis. Linear regression was investigated in terms of r_{Ks} for each pH and individual soil using the statistical program Minitab V.17 (Figure 5.3). From these data, a generalised r_2 function was also formed using the same approach as Šimůnek and Suarez (1997), based on the results of r_{Ks} of soils used in this study of Ali et al. (2019a), and presented in (Figure 5.1 and Figure 5.2). This new generalised function is presented in Equation 5.10, and the statistical parameters are presented in Table 5.2.

$$r_2(\mathrm{pH}) = \begin{cases} 1.0 & \text{for } pH < 7.2 \\ 2.242 - 0.172pH & \text{for } 7.2 \leq pH \leq 9.5 \\ 0.60 & \text{for } pH > 9.5 \end{cases}$$ **Equation 5.10**

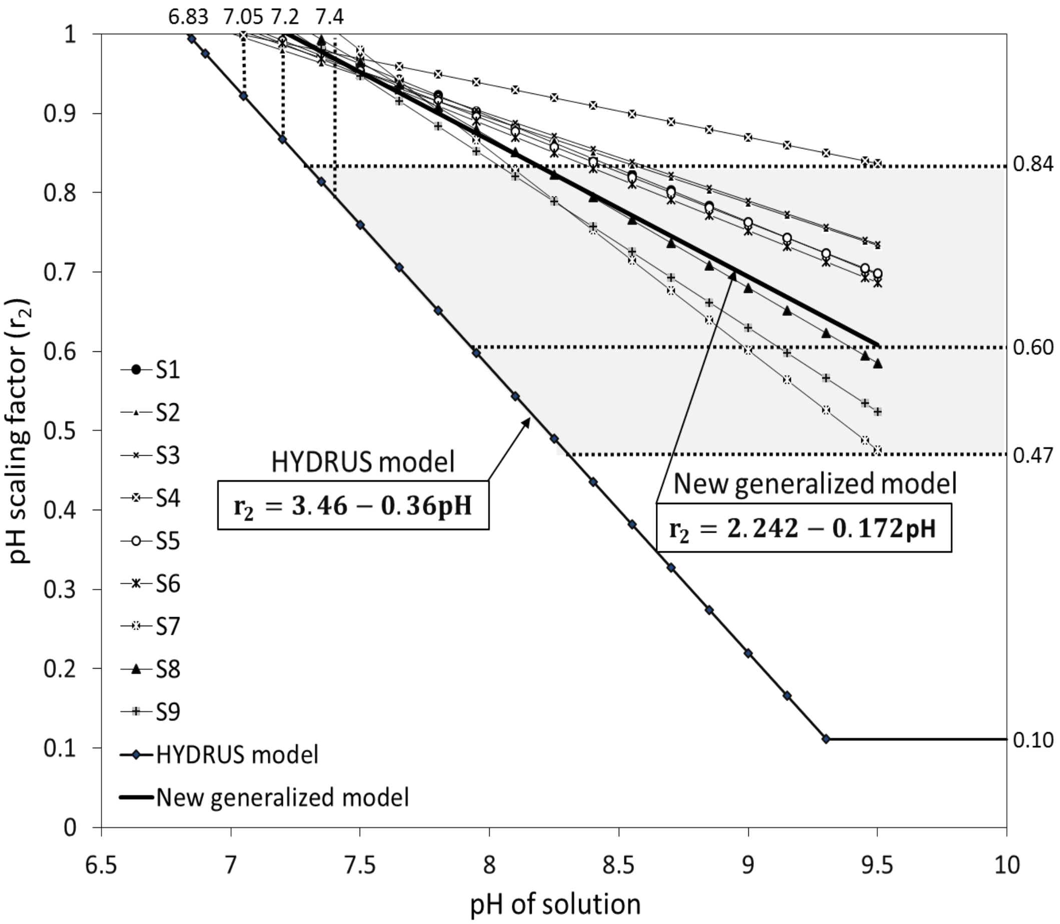

Figure 5.3 The new generalised function and HYDRUS K-pH-dependent function to calculate the hydraulic conductivity scaling factor (r_2) due to the pH of the solution. The shaded region represents the range of variations for the r_2=1.0 and r_2=0.1 conditions for the nine soils in comparison to the HYDRUS K-pH-reduction function; the central dotted line represents the r_1 and r_2 conditions for the generalised equation of these same nine soils.

Table 5.2 Statistical parameters for the HYDRUS pH reduction function, and the generalised function calculated in this study using a linear regression analysis. S is the standard error of the regression, DWS is Durbin-Watson statistics to detect the presence of autocorrelation, and RMSE is the root mean square error. R^2, R^2_{ADJ}, and R^2_{PRED} are the coefficient of determination, adjusted coefficient of determination, and predicted coefficient of determination, respectively. F_{value} and P_{value} are statistic tests to determine whether the term is associated with the response.

Equations	*S*	*DWS*	*RMSE*	R^2	R^2_{ADJ}	R^2_{PRED}	F_{value}	P_{value}
HYDRUS K-pH-dependent function	0.53	2.14	0.78	0.36	0.33	0.22	14.3	0.001
New Generalised Function	0.17	2.14	0.2	0.56	0.55	0.52	59.2	<0.001

In the text below, we will refer to this model as the new generalised model.

5.4.2. Nonlinear regression using Levenberg-Marquardt method

After calculating the parameters for Equation 5.9, by comparison of the K_s reduction data, a stepwise regression was then performed with solution-pH, solution-EC, soil-pH and clay content included. As a result of this, soil-pH was dropped from the model, with the remaining parameters significant and included in the model. Therefore, the solution-pH, solution-EC and clay content were included in a nonlinear forecast model based upon observed training data using the statistical program Minitab V.17.

To find the coefficients of the nonlinear equation expressing pH dependency of the soil K_s reduction, a Levenberg-Marquardt simulation optimisation algorithm (Marquardt, 1963) was employed, which served to iteratively solve an optimisation problem of minimizing errors between the observed and computed values of the K_s reduction in relation to changes of pH and EC of the solution and the clay content percentage of the soils. This optimisation was used to develop a prediction model for forward solutions. This approach works well in modelling situations because it specifically simulates the K_s reduction, due to pH of irrigation water, and is amenable to continuous and adaptive solution-EC, solution-pH and soil clay content, which is extremely desirable in governing K_s temporal and spatial dynamics (Benson & Trast, 1995; Frenkel et al., 1978). The r_2 scaling factor model, based on the Levenberg-Marquardt approach is presented in Equation 5.11, and the model parameters and associated statistics are presented Table 5.3:

$$r_{LM} = \frac{1.25 - pH \times ln(EC)}{(21.72 - 7.42 \times pH + 28.8 \times ln(EC) + 0.33 \times CC)} \qquad \textbf{Equation 5.11}$$

where r_{LM} is the predicted scaling factor for K_s reduction due to the pH of the percolating solution (pH), in tandem with the solution-EC (*EC*) and clay content (*CC*); *EC* is measured in mmol$_c$ L^{-1}, while *CC* is a percentage of the total soil particle size analysis. In the text below, we will refer to this model as the nonlinear model.

Table 5.3 Statistical characteristics pertaining to Equation 5.11 from the nonlinear regression analysis using Levenberg-Marquardt algorithm. SSE is the sum of squared errors, DFE is the error degrees of freedom, MSE is the mean square error, S is the standard error, DF is the degree of freedom, and SS is the sum of squared deviations. F$_{value}$ and P$_{value}$ are statistic tests to determine whether the term is associated with the response that include the predictors in the current model. The α1– α5 are coefficient estimates to describe the relationship between the response (r$_{LM}$) and the predictors (pH, EC and clay content).

Statistic	*Parameters*	*Equation 5.11*			
Summary	Iterations	24			
	Final SSE	5.64			
	DFE	427			
	MSE	0.013			
	S	0.11			
Lack of Fit	DF	211			
	SS	2.759			
	MS	0.013			
	F$_{value}$	0.98			
	P$_{value}$	0.56			
		Parameter Estimates			
	Coefficients	***Estimate***	***SE Estimate***	***Confidence Interval 95% CI***	
				Lower limit	***Upper limit***
Coefficients	α_1	1.25	0.033	1.196	1.31
	α_2	21.72	9.63	6.91	40.1
	α_3	-7.42	1.58	-10.76	-4.95
	α_4	28.76	2.96	24.0	34.54
	α_5	0.33	0.056	0.23	0.45

5.5. Evaluation of the developed models

The models were trained and evaluated against the measured K_s reduction data obtained for nine Australian contrasting soils at four different pH levels (Figure 5.1 and Figure 5.2). The observed r_{Ks} were compared to the predicted r_{Ks} of the corresponding HYDRUS K-pH-dependent function, the new generalised model, and the nonlinear model developed by using the Levenberg-Marquardt optimisation approach; r_{Ks} were calculated using Equation 5.8.

For the nonlinear model, the standard error, the root mean square error (RMSE), and the coefficient of determination (R^2) of both predicted and measured results were compared and slightly diverged from each other, and showed a higher coefficient of determination (R^2=0.82, and T_{test}=2.45) between the observed values and model simulated r_{Ks} than current HYDRUS and new generalised functions. Conversely, the HYDRUS K-pH-dependent model produced the highest standard error and the RMSE, and the lowest coefficient of determination (R^2=0.51, and T_{test}=8.45) in comparison to the new generalised and nonlinear models for observed and simulated r_{Ks} values (Table 5.4).

Table 5.4 Summary statistical characteristics of the observed r_{Ks} and predicted r_{Ks} using HYDRUS K-pH-dependent model, the new generalised model and the nonlinear model, which are shown in Figure 4 using the analysis of variance and the t-test methods.

Equations	***HYDRUS K-pH-dependent Function***	***New Generalised Function***	***Nonlinear Function***
S	0.25	0.17	0.14
RMSE	0.32	0.18	0.16
R^2	0.51	0.77	0.81
R	0.72	0.88	0.90
T test	8.45	2.86	2.45
F_{value}	71.35	8.16	6.01
P_{value}	<0.001	0.005	0.015

The statistical analysis was also conducted among predicted r_{Ks} for the HYDRUS K-pH-dependent function, the new generalised model, and the nonlinear function. A significant difference was observed ($P_{\text{value}}<0.001$) for the new generalised model and the nonlinear equation in comparison to the HYDRUS K-pH-dependent function. While no significant difference was detected ($P_{\text{value}}=0.71$) between predicted r_{Ks} for the generalised and nonlinear equations. These statistics indicate that there was a better fit by the nonlinear model to the observed r_{Ks} data.

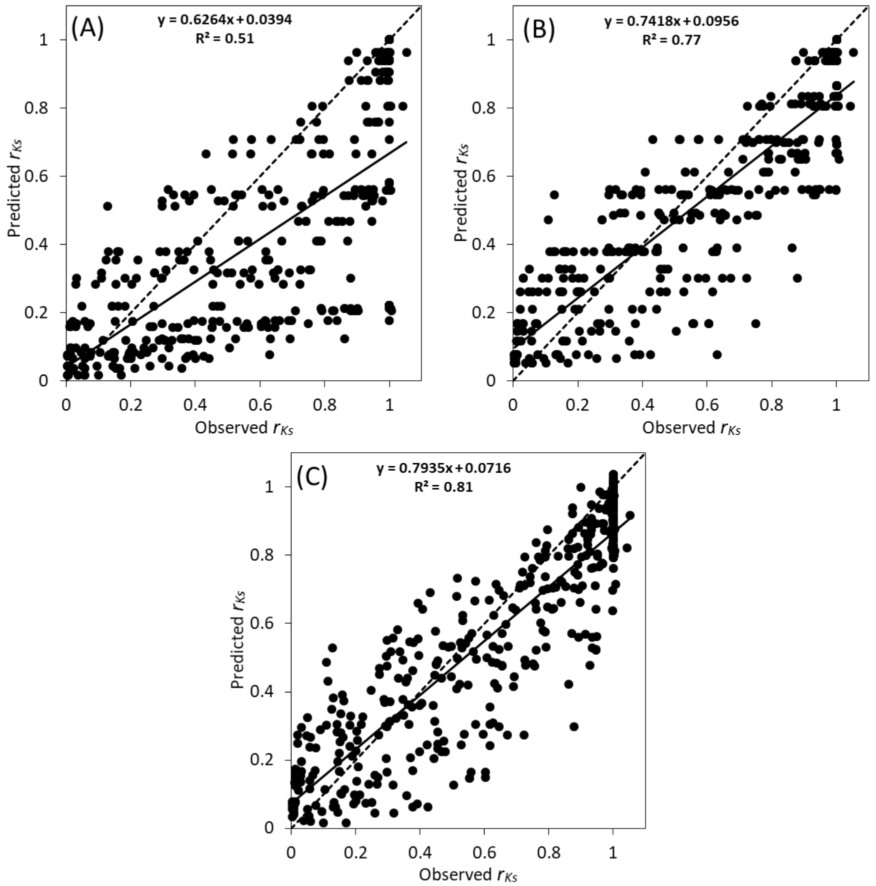

Figure 5.4 The relation between observed r_{Ks} and r_{Ks} predicted using A) the HYDRUS K-pH-dependent model, B) the new generalised model, and C) the nonlinear function (Levenberg-Marquardt algorithm). The diagonal dotted line represents the 1:1 line, and the solid line is the regression fit for the observed data.

5.6. Validation of the new scaling factors

The two new regression models were validated against the experimentally observed r_{Ks} values of the Californian soils from the study of Suarez et al. (1984) (Figure 5.5). Additionally, the HYDRUS K-pH-dependent model (Šimůnek & Suarez, 1997)– developed from the Suarez et al. (1984) data – was evaluated against the same Californian dataset in order to determine the magnitude of improvement the new models provided. Statistical parameters for the observed versus predicted values for each model are presented in Table 5.4.

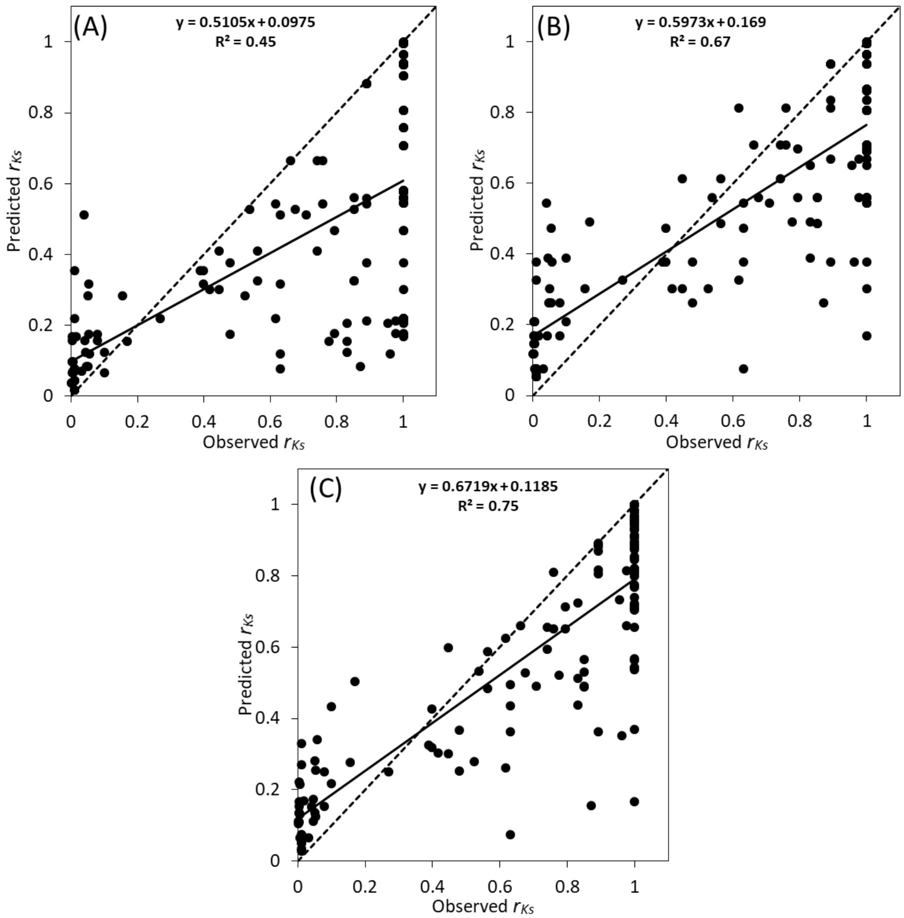

Figure 5.5 The relation between observed r_{Ks} from the study of Suarez et al. (1984) and predicted r_{Ks} using A) the HYDRUS K-pH-dependent model, B) the new generalised model, and C) the nonlinear model (Levenberg-Marquardt algorithm). The diagonal dotted line represents the 1:1 line, and the solid line is the regression fit for the observed data.

Using the T_{test} and the analysis of variance for the null hypothesis of no difference, the statistical tests showed that there was a significant difference between predicted and measured values of r_{Ks} using the HYDRUS K-pH-dependent model (T_{test} = 5.1, $P_{\text{value}}<0.001$, $R^2=0.45$). A comparison was also made between the newly proposed generalised and nonlinear models and the observed r_{Ks} values of Suarez et al. (1984), providing T_{test}=2.15, $P_{\text{value}}<0.034$, $R^2=0.67$ and T_{test}=2.13, $P_{\text{value}}<0.035$, $R^2=0.75$, respectively. The tests indicated that there was a higher correlation between predicted and observed r_{Ks} values for these models in comparison to the HYDRUS K-pH-dependent function at the 0.05 probability level (Table 5.5). The statistics also showed a significant difference ($P_{\text{value}}<0.001$) for the proposed generalised and nonlinear equations for the data from Suarez et al. (1984)'s soils in comparison to the HYDRUS K-pH-dependent model; no significant difference was detected ($P_{\text{value}}=0.93$) between predicted r_{Ks} of the generalised and nonlinear models.

Figure 5.4 and Figure 5.5 indicate that the r_{Ks} data points are consistently better predicted using the new nonlinear equation, although the new generalised linear equation performs reasonably well in comparison. Interestingly, the HYDRUS K-pH-dependent model does not perform well on the data it was created from. We propose that the better performance of the nonlinear equation suggests that soil-specific attributes of soils will be important in explaining the reduction in hydraulic dynamics. This result is not surprising, given the literature indicating that soil hydraulic reduction is soil-specific (Bennett et al., 2019a; Marchuk & Rengasamy, 2011), but it does reinforce the need to update such parameters within soil-water models.

Table 5.5 Summary statistical characteristics of the observed r_{Ks} from the study of Suarez et al. (1984) and predicted r_{Ks} using the HYDRUS K-pH-dependent model, the newly developed generalised equation, and the nonlinear equation, which are shown in Figure 5.5, using the analysis of variance and the t test methods.

Equations	***HYDRUS K-pH-dependent Function***	***New Generalised Function***	***Nonlinear Function***
S	0.30	0.24	0.20
RMSE	0.37	0.25	0.22
R^2	0.45	0.67	0.75
R	0.67	0.82	0.86
T test	5.1	2.15	2.13
F_{value}	25.77	4.5	4.4
P_{value}	<0.001	0.034	0.035

5.6.1. Observed versus predicted reduction in hydraulic conductivity

The statistical analysis showed the accuracy of the predicted r_{Ks} for each model for each dataset (Table 5.4 and Table 5.5). For r_2 optimisation, the new generalised and nonlinear models demonstrated better performance, as indicated by their lower RMSE and T_{test}, and higher coefficient of determination values for the Australian and Californian soils. For both data sets, when the nonlinear model was used, the predicted outcomes were generally in closer agreement with the observations of r_{Ks} than the other two models.

Naturally, the observed r_{Ks} values are dependent on the EC, SAR, and pH of the solution, as well as the soil clay content and mineralogy (Bennett et al., 2019a; McNeal & Coleman, 1966; Suarez et al., 1984). The relatively high accuracy and performance of the nonlinear model was mainly due to its capability to predict pH effects more specifically by considering electrolyte concentration and clay content. The r_2 scaling factor for the nonlinear model ($r_{2_{LM}}$) is mainly controlled by pH and EC of the solution and the clay content of the soil, as shown in Equation 5.12. Comparatively, the r_2 scaling factor for the generalised models is simply based on the pH of the solution (Equation 5.2). Accordingly, the predicted r_{Ks} values were calculated using Equation 5.5 and Equation 5.13 to calculate the r_{Ks} of the generalised models and nonlinear model, respectively.

$$K_{LM}(h, pH, SAR, EC, CC) = r_{LM}(pH, SAR, EC, CC)\ K_S\, K_r(h) \qquad \textbf{Equation 5.12}$$

$$r_{LM}(pH, SAR, EC, CC) = r_1(SAR, EC)\, r_{2_{LM}}(\text{pH, EC, CC}) \qquad \textbf{Equation 5.13}$$

where K_{LM} is the hydraulic conductivity based on the Levenberg-Marquardt nonlinear model (r_{2LM}; Equation 5.11), r_{LM} is the saturated hydraulic conductivity reduction as a result of adverse effects of EC, SAR, and pH (using the nonlinear function) and CC is the percentage of clay content.

Another limitation of the predicted hydraulic conductivity is that final r_{Ks} is also dependent on the degradative effects of EC and SAR (r_1; Equation 5.3). The r_1 scaling factor has been generalised and determined empirically and its parameter values developed using only a narrow range of soils. In that matter, the use of generalised parameters would increase errors related to the uncertainty in the weighted scaling factors and result in reducing the accuracy of r_{Ks} prediction. The extent of uncertainty of the pH scaling factor ($r_{2_{LM}}$) is somewhat reduced by including EC and clay content in the calculation of the scaling factor for the hydraulic dynamic reduction (Equation 5.13). This is a clear indication of the improvement of r_{Ks} prediction using the nonlinear function, although it could be further improved by combining r_1 and r_2 in a single non-linear equation.

5.7. Discussion

5.7.1. Improvement of HYDRUS

The literature demonstrates that the HYDRUS models have been effectively applied to laboratory and field experiments (Ramos et al., 2011; Ramos et al., 2012; Rasouli et al., 2013) using soil hydraulic conductivity and solute transport model parameters. Šimunek et al. (2012) argue that the HYDRUS codes are physically based models and may require little or no calibration when all required input parameters are experimentally determined. However, in terms of hydraulic conductivity dynamic decline, there is no physical parameter that can be measured, and the functions describing reduction do not allow for soil-specific nuances. This is an important limitation of the current HYDRUS model family and modules. Our work suggests that an updated generalised equation could be utilised, but it also further suggests that the inclusion of soil-specific attributes could provide a consistently better relation between observed and predicted results, which supports the use of and further development of the non-linear function.

Using a broad range of soils, the principal goal of this current study was to evaluate the existing scaling factor (r_2) and its applicability, with the intent of improving upon the existing HYDRUS reduction function to include soil specific attributes. We have demonstrated that the generalised equation for the r_2 scaling factor of the HYDRUS model leads to a unique solution and can be updated using a broader range of soils. This allows for forming of soil-specific based equations, in which the predicted r_{Ks} values are compared to observed r_{Ks} values for the 12 examined soils of Australia and California (Figure 5.4 and Figure 5.5). While the new generalised equation provided reasonable results over the existing linear HYDRUS equation, the nonlinear validated approach for K_s reduction will provide more confidence in the ability of the HYDRUS model to estimate dynamic K_s reduction. Soils are inherently heterogeneous in their properties and their resiliency to retain soil structure under conditions such as alkaline pH, low solution salinity, and adverse monovalent cation concentrations varies. The Levenberg-Marquardt optimisation allows for inclusion of multiple factors in a manner that provides a better fit to the complex non-linear dynamics of soil hydraulic reduction.

5.7.2. Nonlinear performance and future directions

The nonlinear inverse modelling included additional parameters, such as solution EC and soil clay content, which are critical governing factors in the management of the extent of K_s reduction (Agassi et al., 1981; Cook et al., 2006; Dang et al., 2018b; Dang et al., 2018d; Zhu et al., 2016). An increase in EC generates the osmotic pressure that compresses the diffuse double layer repulsive effect on the clay domains (Quirk 2001), subsequently diminishing the contribution of pH and SAR on the diffuse double layer expansion (Sumner, 1993). The clay content is also an important factor in determining the extent of the hydraulic conductivity reduction, and subsequently the resilience of the soil structure stability (Bennett et al., 2019a). Concomitantly, the clay content of a soil has also been documented to affect the resilience of soil structure to the pH of the applied solution (Lieffering & McLay, 1996; Nyamangara et al., 2007). For lower clay content soils, the absolute decrease in K_s is greater compared to clay soils, indicating the potential for negative effects of pH on K_s (Lieffering & McLay, 1996; Suarez et al., 1984). A similar trend was observed for K_s reduction in this study. Furthermore, in terms of the percent relative hydraulic reduction, clay content will have an effect, whereby highly sandy soils may require complete dispersion of the existing clay to cause a percent reduction in K_s equivalent to disaggregation properties in highly clay dominant soils. This is considered as a function of the greater frequency of pores with smaller pore diameter, and clay domain swelling without dispersion where sufficient clay exists. However, the agreement between the observed and predicted results for the nonlinear equation suggests there is still requirement for improvement in predictive capability.

Bennett et al. (2019a) suggested that soil-specific hydraulic conductivity reduction functions require the consideration of clay properties, especially the quantification of clay mineral type, size, and surface charge, which reinforces the assertions of Quirk (2001). Additionally, and related to the clay specificity, the concept of ionicity affecting the net negative charge (Marchuk & Rengasamy, 2011) is also required to be incorporated into a soil-specific structural model (Bennett et al., 2019a). Heterogeneous properties and the soil specific behaviour under pH of applied solutions are known to affect the net negative charge (Chorom et al., 1994), and thereby provide a means of improving the prediction of hydraulic conductivity reduction.

It is also important to reflect on the fact that this study, and the study of Suarez, et al. (1984)—the existing pH hydraulic reduction function within HYDRUS—examined repacked soil cores, rather than undisturbed soils. This was to avoid heterogeneity factors that potentially mask the process effect of the mechanisms controlling hydraulic reduction. Importantly, we contend that the mechanisms controlling hydraulic conductivity reduction dynamics within a pore are consistent across all pore size ranges in both saturated and unsaturated conditions. This means that the scaling factor would apply uniformly to all pore sizes, but that the absolute differences in hydraulic conductivity would depend on the pore size, inferring that the results in this study are applicable to both saturated and unsaturated conditions. However, the effect of pH on the hydraulic dynamics in unsaturated soil was outside the scope of the current study, and would be prudent to validate in future work.

Furthermore, there is merit in moving away from a scaling factor model that seeks to separate the cation and pH effects. Even with the improvement of the nonlinear model by including EC, it still fails to include the effects of cations on the dispersive, and thus hydraulic conductivity reductive, effects of SAR. The current dataset is insufficient to achieve this, with only two SAR levels, however it does indicate that such a model can be achieved with reasonable confidence, given sufficient data. The level of confidence is an important topic to consider also. Bennett et al. (2019a) demonstrated that a generalised equation for the soil-specific threshold electrolyte concentration (C_{TH}) varied by ≈±7.5 SAR units within one standard deviation, concluding that this level of variation within a generalised equation was not reliable, and was environmentally unsound. However, the current scaling factor within HYDRUS is worse. The Ezlit et al. (2013) disaggregation model, which the Bennett et al. (2019a) work is based upon, was an improvement on the HYDRUS EC and SAR based reduction model (i.e. McNeal, 1968). On this basis, the first step would be to improve the current nonlinear approach to include the SAR effects within it, and then incorporate this into HYDRUS, with a level of confidence surrounding the output for the user. Simultaneously, there is a requirement to improve predictive capability from a fundamental point of view.

5.7.3. Soil initial pH and hydraulic conductivity reduction

The soil initial pH was dropped from the stepwise regression process, which led us to not include it within our models. This may suggest that the initial soil pH is not important in predicting hydraulic conductivity decline. However, we caution this assumption on the basis of Ali et al. (2019a) who demonstrated that the initial soil pH and the clay content were both important in controlling the extent of hydraulic conductivity reduction. The same nine soils were used in this work. It was observed by Ali et al. (2019a) that while there was a significant reduction in soil structural characteristics for alkaline soils as pH increased, that the concomitant extent of K_s reduction was not significant, although it consistently decreased as pH increased. That is, the size of the reduction effect appeared to be controlled by the initial soil pH. The contrasting situation for acidic initial soil pH interacted with lower clay content, and as this current work shows, outweighed in terms of the effect of clay content. For this reason, and the fact that the updated models are still only developed on 12 soils, it would be prudent to extend these studies to a broader range of soils that have varying pH and varying clay content within each pH subclass. As far as the authors are aware, combining of the nine Australian soils and three Californian soils constitutes the most comprehensive dataset to determine the pH effect on soil hydraulic conductivity, which clearly identifies the requirement to increase the dataset such that the soil- specificity is better captured within the non-linear coefficients. This should further improve the nonlinear approach.

5.8. Conclusion

This research identified the limitation of the HYDRUS scaling factor (r_2) model and developed and validated two new models to optimise saturated hydraulic conductivity prediction. The proposed models were produced using a similar approach as in the HYDRUS model, with a nonlinear regression method further implemented. The nonlinear equation developed using the Levenberg-Marquardt algorithm considers pH and EC of the solution, as well as the soil clay content, which is an important improvement towards soil-specific pedotransfer functions that may be incorporated into HYDRUS. The overall performance of the new models was significantly better than that of the existing linear HYDRUS hydraulic reduction scaling model. This was the case for both the current Australian data set and for the Californian data set that the HYDRUS model was based upon.

Even though the prediction of the reduction in the hydraulic conductivity still has room for improvement in terms of the size of the dataset and soil types that control hydraulic conductivity reduction scaling factors and coefficients within the non-linear model, the results significantly build upon the existing circumstance. The nonlinear model, developed using the Levenberg-Marquardt approach to substitute the r_2 scaling factor in the HYDRUS program, provides a consistently more accurate estimate of the hydraulic conductivity than the current HYDRUS r_2 reduction model. Furthermore, the nonlinear equation is put forward as the basis for further improvement for the incorporation of identified soil properties, and suggested, to govern soil structural dynamics.

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6. Assessing the hydraulic reduction performance of HYDRUS-1D for application of alkaline irrigation in variably-saturated soils: Validation of pH driven hydraulic reduction scaling factors

Abstract

Land application of alkaline irrigation water is an increasing practice in most agricultural lands around the world due to the shortage of freshwater resources. Accurate evaluation of the effects of alkalinity on soil properties is essential to avoid environmental risks. In this study, we used long leaching columns to evaluate alkalinisation and sodification hazards in the soil profile in the laboratory condition at different levels of alkaline water quality of 0, 100, 310 and 650 (HCO_3^-, mg L^{-1}) with electrical conductivity (EC)≈2.1 dS m^{-1} and sodium adsorption ratio (SAR) ≈12 (mmol_c $L^{-1})^{0.5}$. The ability of the HYDRUS-1D model was also assessed to simulate solute and water movement under the unsaturated condition in columns of 40 cm height filled with acidic, neutral or alkaline soils. Changes in soil EC, SAR, pH and alkalinity were monitored at 5, 15, 25 and 35 cm depths for 290 days. Increased solution alkalinity resulted in increased pH, alkalinity and sodicity within the soil profile, in particular for the soil surface and acidic soils. In general, the HYDRUS model, using the standard hydraulic reduction scaling factor, was able to simulate the effects of alkalinity in the soil profile and the associated hydraulic conductivity reduction. Amending the pH driven hydraulic reduction scaling factor to a non-linear, soil-specific, pedotransfer function significantly improved the correlation between predicted and observed hydraulic conductivity. The findings of this study provide validation for a non-linear approach towards determining the pH hydraulic reduction scaling factor in the HYDRUS-1D model for unsaturated conditions. However, it is noted that further improvement of this non-linear approach is required to incorporate other factors governing soil structural stability.

Keywords: Alkalinity, unsaturated condition, sodicity, hydraulic conductivity, solute movement, HYDRUS-1D

6.1. Introduction

Marginal quality water has become an alternative source of water for irrigation purposes in most agricultural lands, due to the scarcity of freshwater. These are usually alkaline, sodic and saline water, and requires proper consideration prior to and during application to lands (Ali et al., 2019a; Raine & Ezlit, 2007). Increased water use efficiency can also lead to increasing alkalinity, sodicity and salinity problems due to insufficient leaching (Raine et al., 2007; Rengasamy, 2010). The transport of solutes and the accumulation of these salts and their interactions may cause a significant decrease in the agricultural productivity of irrigated lands (Ezlit et al., 2010; Minhas & Gupta, 1993).

The interaction between cations and anions and mechanisms of solute transport in the root zone in unsaturated conditions are assumed to be appropriately estimated using models that simulate simultaneously water flow and solute transport processes (Šimůnek & Suarez, 1997). Solute transport processes throughout the unsaturated zone are closely associated with soil types and soil properties (Nielsen & Biggar, 1986) and a complex, highly variable and non-linear process in terms of chemical and hydraulic dynamics that are taking place in the soil-plant systems (Van Genuchten & Šimůnek, 1996). Analytical and mathematical models of the flow and solute transport processes are being used for simulating subsurface flow and transport processes for soil and water management. These models are numerically solving the Richards equation for flux and analytical and numerical solution of the Fickian convection-dispersion equation for the transport of solutes (Gonçalves et al., 2006). These conventional models are important tools for simulating flow and solute movement in the soil for laboratory and field experiments associated with the unsaturated flow and solute movement (Šimůnek et al., 2007).

The HYDRUS-1D software package is one of the mathematical models commonly being used for simulation of the water flow and transport of various chemicals involved and is widely employed model worldwide (Šimunek et al., 2012). The HYDRUS model has been used to simulate the transport of solutes in the soil solution and wastewater effects on soil hydraulic properties (Assouline & Narkis, 2011), mineral nitrogen species (Li et al., 2015), saline and sodic water in soil (Gonçalves et al., 2006), and use of soil amendments (Reading et al., 2012; Shaygan et al., 2018; Wang et al., 2016).The model numerically solves the Richards equation (Richards 1931) for variably saturated water flow, heat and solute transport. Within HYDRUS, the hydraulic conductivity reduction function is based on the study of McNeal (1968) for salt concentration and exchangeable sodium percentage and the study of Suarez et al. (1984) for the pH of the solution. These factors are treated as two independent scaling factors that multiply to produce the ultimate scaling factor used for hydraulic reduction. These effects were further studied by Ezlit et al. (2013) and Dang et al. (2018a). The salt concentration, exchangeable sodium percentage (ESP) and pH of solutions are considered as the main parameters in the HYDRUS model that affect the hydraulic dynamics (Šimůnek et al., 1998). The hydraulic conductivity (*K*) is expected to be affected when the soil solution is below optimum conditions, causing swelling, dispersion and disaggregation (Bennett et al., 2019a; Ezlit et al., 2013; Šimůnek & Suarez, 1997). The current optimum condition for salinity of soil solution is 300 $\mathrm{mmol_c\ L^{-1}}$ and pH as low as 6.83 (Šimůnek & Suarez, 1997). The effects of salinity, sodicity and pH on the disaggregation model for saturated hydraulic conductivity (K_s) reduction were further studied to enhance the understanding of soil specific responses (Ali et al., 2019a; Bennett et al., 2019a; Dang et al., 2018a). Regarding the solution pH, Ali et al. (2019a) indicated that the clay content and initial soil pH are important parameters to control the extent of hydraulic conductivity reduction.

Thus, a further understanding of the mechanisms of alkaline irrigation water, solute movement, and the complex mechanisms associated with alkalinity in soil under unsaturated conditions are crucial in managing soil and water alkalinity. It is also important to evaluate the current HYDRUS scaling factor (r_2), as well as the recently developed generalised and non-linear function, in terms of changes in hydraulic dynamics, due to the pH of solutions (Ali et al., 2019a). Therefore, this study was carried out to evaluate the developed generalised and non-linear models for prediction of hydraulic conductivity dynamics in variably saturated conditions using laboratory column experiments, and to provide a practical assessment of HYDRUS on the basis of its potential to plan for land application of alkaline irrigation water in laboratory conditions. The work hypothesises that the use of updated hydraulic reduction scaling factors will significantly improve the accuracy of the HYDRUS model, in particular, that a soil specific (non-linear) approach will outperform a generalised approach.

6.2. Material and methods

6.2.1. Soil chemical and physical measurement

Soil samples were collected from three sites (Maryborough-QLD, Dalby-QLD and Eldorado-NSW) from 0 to 30 cm depth. The soils were air dried and carefully crushed with sufficient energy to breakdown the aggregates to pass through a 2 mm sieve; care was taken to not apply energy greater than required to maintain the physical bonds of the aggregates <2 mm. These soils were selected based on their contrasting properties such as clay mineralogy, clay content and initial alkalinity, and are a subset of those used by Ali et al. (2019a) to develop the non-linear function assessed here. Using standard methods from Rayment and Lyons (2011), the electrical conductivity (Method 3A1) and pH (Method 4A1) were measured on a 1:5 soil water mix. The alkalinity was determined using a Radiometer Analytical Titrator (TIM845, Titration Manager). Published methodologies were used to determine clay mineralogy by X-ray diffraction (Jackson, 2005), soil particle size distribution (Gee & Bauder, 1986) and organic carbon (Walkley & Black, 1934). The soluble and exchangeable cations were measured based on the method 15A2 from Rayment and Lyons (2011). Soils were pre-treated with deionised water (EC ≈ 5 µS/cm, pH=7) to remove soluble salts and then supernatants were decanted to determine soluble cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+). The exchangeable cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) then were released using 1M NH_4Cl extraction and analysed by inductively coupled plasma atomic mass spectroscopy (Perkin Elmer Nexion ICP-MS). The soil characteristics are presented in Table 6.1.

The water retention curve parameters were determined by a hanging water column for each soil type. Air dried soils were packed (65 cm^3, 2 cm height) in sintered funnels at a bulk density of 1.27, 1.29 and 1.35 g cm^{-3} for Soil 1, Soil 2 and Soil 3, respectively. The packed soils were equilibrated with water to reach saturation point (0 cm head) and samples were then subjected to negative pressure heads of 0–150 cm head (0–15 kPa). The change in water content was logged for each negative pressure increment (Dane & Hopmans, 2002).

Table 6.1 soil physical and chemical properties of selected soils.

Properties	*Unit*	*Soil 1*	*Soil 2*	*Soil 3*
pH (1:5)		4.5	7.4	8.8
EC (1:5)	dS m-1	0.08	0.21	0.30
Total alkalinity	mg L-1	0.0	55	157.1
SAR	(mmolc L-1)0.5	0.9	0.96	4.3
CROSS	(mmolc L-1)0.5	1.2	1.12	4.6
ESP	%	3.2	7.89	17.5
EDP	%	5.2	9.4	21.5
CEC	cmolc kg-1	1.8	23.2	15.4
Clay activity ratio	cmolc. g clay-1	0.12	0.45	0.45
Organic carbon	%	1.5	1.01	1.6
Clay	%	15	52	34
Texture		Loam	Clay	Clay loam
Australian taxonomic class†		Grey Kurosol	Black Vertosol	Red Dermosol
USDA soil taxonomic class		Ultisol	Vertisol	Inceptisol
Location in Australia		25°21'36"S, 152°44'40.44"E Maryborough, QLD	27°13'48.0"S, 151°19'12.0"E Dalby, QLD	28°54'50.48"S, 150°16'18.6"E Eldorado, NSW

† Australian Soil Classification (Isbell & NCST, 2016)

For residual (θ_r) and saturated (θ_s) water content determination, the soils were packed into polyvinyl chloride (PVC) cylinders (50 mm inner diameter) for 40 mm depth, with mesh bottoms for drainage. The soils were then immersed into the water until two-thirds of the soil sample was immersed; this allowed wetting from the bottom up overnight, eliminating the air contained in soil pores and reaching saturation point. Subsequent to saturation, these soils were weighed; oven dried for 48 h at 105°C, reweighed, and θ_s was calculated. The residual water contents for soils were determined after an extended period of air drying under laboratory condition for 3 weeks (Miller et al., 2002). The samples then were dried at 105°C in the oven for 48 h to determine gravimetric residual water content (i.e. air-dry moisture content (ADMC).

The initial hydraulic conductivity of soils was measured using the constant head saturated hydraulic conductivity (K_s) (Klute, 1965). Soil samples were carefully packed into PVC cylinders (87.5 mm inner-diameter), with mesh bottoms for drainage, to a depth of 10 cm and attaining a mean bulk density of 1.27, 1.29 and 1.35 ±0.02 g cm^{-3} for Soil 1, Soil 2 and Soil 3, respectively. A calcium chloride solution (EC=2 dS m^{-1}; $CaCl_2.2H_2O$) was used to leach soil columns to determine initial K_s of soils (Bennett et al., 2019a; Ezlit et al., 2013).

6.2.2. Experimental design:

The air-dried and sieved soils were packed into the laboratory columns to form 40 cm depth (Figure 6.1) to investigate the water and solute transport within the soil profiles. The experimental columns were 500 mm PVC cylinders with an inner diameter of 87.5 mm. The solutions were applied to soils using regulated drippers to obtain partially saturated water content during experimentation with a flow rate of 0.15 L hr^{-1}. Porous microfiber tubes (0.2–100 µm porosity and 0.6 mm inner-diameter) were installed in different depths of soil columns to extract the soil solution; soil moisture sensors were also installed to monitor water content during experimentation. Resistive soil moisture sensors were connected to Arduino computer chips and calibrated for each used soil, using gravimetric water content determination. Soil moisture probes and microfiber filter tubes were installed at 5, 15, 25, and 35 cm depths to monitor moisture content and extract the soil solution. The experiment consisted of four solutions with bicarbonate alkalinity of 0, 100, 310 and 650 mg L^{-1}. SAR was 12 ($mmol_c$ $L^{-1})^{0.5}$ and EC was 2.1 dS m^{-1} for all solutions (Table 6.2). Pure sodium bicarbonate ($NaHCO_3$), calcium chloride dihydrate ($CaCl_2.2H_2O$), and sodium chloride (NaCl) and distilled water was used to prepare desired solutions.

Table 6.2 Ionic composition of irrigation waters applied to soils.

Properties	*Solution 1*	*Solution 2*	*Solution 3*	*Solution 4*
pH	6.8	7.3	8.1	8.5
EC (dS m^{-1})	2.08	2.09	2.08	2.09
Alkalinity (HCO_3^-) (mg L^{-1})	0	100	310	650
Calcium (mmol L^{-1})	1.54	1.589	1.509	1.56
Sodium (mmol L^{-1})	14.99	15.33	15.5	15.55
Chloride (mmol L^{-1})	18	16.96	13.44	7.31
SAR ($mmol_c$ $L^{-1})^{0.5}$	12.09	12.14	12.6	12.4

Plastic mesh and a filter paper were placed at the bottom for drainage of each column. The columns were carefully filled with sieved soils to attain the mean dry bulk density of 1.26, 1.36 and 1.29 g cm^{-3} for Soil 1, Soil 2 and Soil 3, respectively.

The soil columns were covered with a fast flow filter paper from the top. The solutions were applied from the top with accurately regulated inflow to achieve unsaturated or partially saturated condition. Soil columns have received 11.7 ML ha^{-1} of each solution during experimentation. Soil solutions at depths of 5, 15, 25, and 35 cm were extracted at each time interval (1, 80, 143, 214, 290 days) using microfiber tubes; pH, EC, alkalinity, and cation concentrations of the soil solutions were then measured. At the end of the experiment, soil columns were dismantled, and soil samples were collected from the depths of 0–5, 10–20, 20–30, and 30–40 cm to measure residual and saturation water holding capacity and saturated hydraulic conductivity.

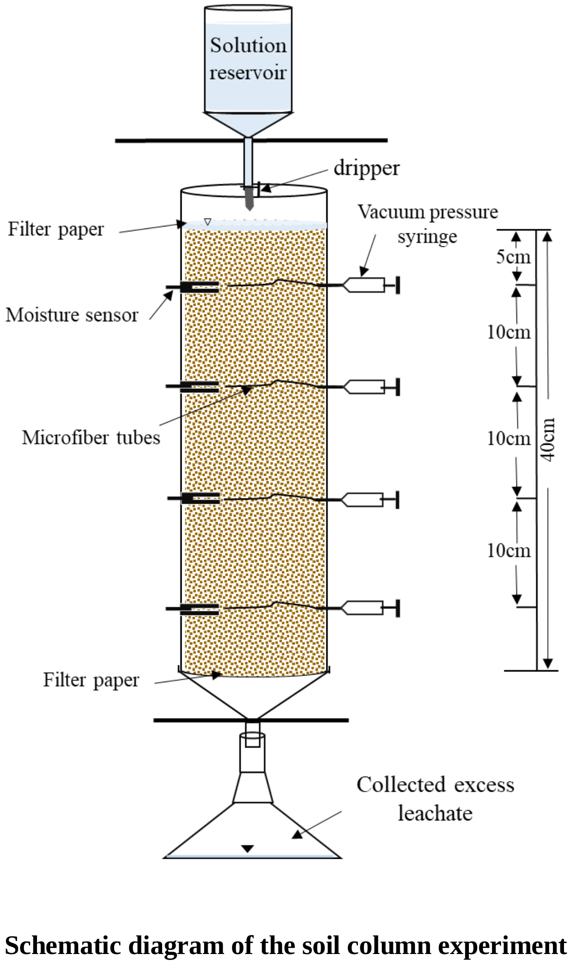

Figure 6.1 Schematic diagram of the soil column experimental design.

6.2.3. Water flow

One dimensional water movement in a partially saturated rigid porous medium is described by an equation modified from the Richard’s equation (Šimůnek et al., 1996) (Equation 6.1).

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left[K\left(\frac{\partial h}{\partial x}+1\right)\right]$$

Equation 6.1

Where h is the water pressure head (L), θ is the volumetric water content (L^3L^{-3}), t is leaching time (minutes), x is the spatial coordinate (positive equivalent to upwards), and K is unsaturated hydraulic conductivity ($L\ T^{-1}$). The Richard’s equation assumes that the effects of the vapour phase is ignored in water flow and accounts only for the liquid phase in the water mass balance.

The HYDRUS model also implements the soil hydraulic conductivity functions of Van Genuchten (1980) who used the statistical pore size distribution model of Mualem (1976) to obtain a predictive equation for the unsaturated hydraulic conductivity function in terms of soil water retention parameters. The analytical expression of Van Genuchten (1980) for the soil water retention curve for unsaturated hydraulic conductivity is shown in Equation 6.2.

$$K(h) = \begin{cases} K_s K_r(h), & h < 0, \\ K_s, & h \geq 0. \end{cases}$$

Equation 6.2

where $K(h)$ is hydraulic conductivity dynamic function, K_s is saturated hydraulic conductivity, $K_r(h)$ is hydraulic conductivity reduction for a specific head (h). The $K(h)$ for change in ion chemistry is based on the work of McNeal (1968) and Suarez et al. (1984). The hydraulic conductivity reduction is incorporated in the HYDRUS model as a scaling factor (r) that is dependent on the electrical conductivity, ESP, and the pH of the soil solution.

Equation 6.3

$$K(h) = K_s K_r = K_s {S_e}^{l}\left[1-\left(1-{S_e}^{1/m}\right)^{m}\right]^2$$

$$S_e = \frac{\theta(h) - \theta_r}{\theta_s - \theta_r}$$ **Equation 6.4**

Where K_s is the saturated hydraulic conductivity (cm day^{-1}), K_r is the relative hydraulic conductivity, S_e is the effective saturation, m (m=1-1/n, and n>1) and n are shape factors, l is the pore connectivity parameter usually assumed to be 0.5. $\theta(h)$ is the volumetric water content, and θ_r and θ_s are the residual and saturated water content, respectively.

The effect of pH on the soil hydraulic conductivity within the current HYDRUS model was calculated from the experimental data of Suarez et al. (1984). This model includes the reduction functions from experimental data of McNeal (1968) and Suarez et al. (1984). The scaling parameter (*r*) accounts for the effects of solution components such as pH, SAR, and electrolyte concentration that controls hydraulic conductivity (Šimůnek et al., 1996; Šimůnek & Suarez, 1997) (Equation 6.5 and 6.6). The scaling parameter *r* for hydraulic conductivity reduction function is divided into two parts.

$$r(pH, SAR, C_o) = r_1(SAR, C_o)\, r_2(pH)$$ **Equation 6.5**

$$r_2(pH) = \begin{cases} 1.0, & \text{for } pH \leq 6.83 \\ 3.46 - 0.36pH, & \text{for } 6.83 < pH < 9.3 \\ 0.1, & \text{for } pH \geq 9.3 \end{cases}$$ **Equation 6.6**

Where C_o is the total salt concentration, *h* is hydraulic conductivity, and *r* is the scaling parameter that represents the effects of solution composition on the hydraulic conductivity. A value of *r* equal to 1 represents the soil chemistry supporting the maximum hydraulic conductivity condition. The variable r_1 accounts for the effects of exchangeable sodium and concentration of salts on the hydraulic conductivity, while r_2 reflects the effects of solution pH on the hydraulic conductivity. The assumption is that the scaling parameter *r* can be applied for the entire range of pressure head under saturated conditions. Recently, the r_2 scaling factor has been updated from hydraulic conductivity reduction due to pH of applied irrigation water on Australian soils by Ali et al. (2019b). A generic and a soil specific function was developed to replace the original HYDRUS pH scaling factor for hydraulic conductivity reduction due to r_2(pH), as demonstrated in Equation 6.7 and 6.8, respectively.

$$r_2(\mathrm{pH}) = \begin{cases} 1.0 & \text{for } pH < 7.2 \\ 2.242 - 0.172pH & \text{for } 7.2 \leq pH \leq 9.5 \\ 0.60 & \text{for } pH > 9.5 \end{cases} \qquad \textbf{Equation 6.7}$$

$$r_2(\mathrm{pH}) = \frac{1.25 - pH \times ln(C_o)}{(21.72 - 7.42 \times pH + 28.8 \times ln(C_o) + 0.33 \times CC)} \qquad \textbf{Equation 6.8}$$

Where pH is the pH of applied irrigation water, C_o is salt concentration (mmol$_c$ L^{-1}) and CC is the clay content as a percentage in the soil.

6.2.4. Solute transport and chemical reaction modelling

The partial differential equation governing one-dimensional advective-dispersive chemical transport under transient flow in variably saturated soil is calculated as shown in Equation 6.9.

$$\frac{\partial(\theta c_k)}{\partial t} + \rho\,\frac{\partial(\theta \bar{c}_k)}{\partial t} + \rho\,\frac{\partial(\theta \hat{c}_k)}{\partial t} = \frac{\partial}{\partial x}\left(\theta D\,\frac{\partial c_k}{\partial x} - qC_k\right) \qquad k=1, 2, 3 \ldots, n_s \qquad \textbf{Equation 6.9}$$

Where C_k is the total dissolved concentration of aqueous component k, respectively [mg L^{-1}], $\bar{C}_k$, is the total exchangeable of the aqueous concentration (g g^{-1}), $\hat{C}_k$, is non-adsorbed solid phase concentration of the aqueous component (g g^{-1}), ρ is the soil bulk density (g cm^{-3}), D is the dispersion coefficient (cm^2 hr^{-1}), q is the volumetric water flux (cm hr^{-1}), n_s is the number of components, and k is the sum of the concentration of components.

The major ion chemistry component in the HYDRUS model can be used for modelling chemistry scenarios in agriculture because of cation exchange, salt accumulation, and precipitation-dissolution of minerals (including calcite and gypsum). This model is also capable of simulating equilibrium reactions between the solid, and liquid phases, as well as linear equilibrium reactions between the liquid and gaseous phases. The major variables of the chemical system are Ca, Mg, Na, K, SO_4, Cl, NO_3, H_4SiO_4, alkalinity, and CO_2. Alkalinity is modelled as a conventional property to allow for oscillation of CO_2 concentrations (Šimůnek et al., 2013). Two mass balance equations for the total analytical concentration of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) are described as follows:

$$CO_3^T = [CO_3^{2-}] + [CaCO_3^o] + [MgCO_3^o] + [NaCO_3^-]$$

Equation 6.10

$$HCO_3^T = [HCO_3^-] + [CaHCO_3^+] + [MgHCO_3^+] + [NaHCO_3^o]$$

where variables with subscript *T* represent the total analytical concentration in solution of that particular species, and where brackets refer to concentration in molalities (mol kg^{-1}).

$$Alkalinity = 2CO_3^T + HCO_3^T + [\,OH^-] - [H^+]$$

Equation 6.11

6.2.5. Cation Exchange and Selectivity

The partition between the solid and solution phases is described with the Gapon selectivity coefficient (White & Zelazny, 1986) (Equation 6.12).

$$K_{ij} = \frac{\overline{C}_i^{y+}}{\overline{C}_j^{x+}} \frac{(C_j^{x+})^{\frac{1}{x}}}{(C_i^{y+})^{\frac{1}{y}}}$$

Equation 6.12

Where *Kij* is the Gapon selectivity coefficient, *x* and *y* are the valences of species *j* and *i* respectively. *C* is the concentration of the ions in solution, and $\overline{C}$ is the concentration of the exchange phase. The HYDRUS model assumes that the cation exchange capacity (mol_c kg^{-1}) equals to the sum of the exchangeable cations, constant and independent of pH.

$$\overline{C}_T = \sum \overline{C}_i$$

Equation 6.13

6.2.6. Validation of HYDRUS-1D model

In this study, the flow and solute transport processes for unsaturated soils on a laboratory scale was simulated using the HYDRUS-1D program (version 4.17.0140), coupled with the PHREEQC biogeochemical code (HP1) module (Jacques & Šimůnek, 2005). The HP1 module was selected because the major ion chemistry module over-estimated the pH and alkalinity of the solution, especially for acidic soil and zero and low alkalinity solutions (pH > 5.65, and HCO_3^- > 1.5 $mmol_c$ L^{-1}). Moreover, the major ion chemistry does not allow input initial chemistry (e.g. pH and HCO_3^-) for each specific depth throughout the soil profile. The results of leached soil profiles were used for comparison with the results of the HYDRUS-1D model. The aim of validating the HYDRUS-1D model was to test the capability and accuracy of this model to simulate the change in soil properties leached with various levels of alkalinity under variably saturated conditions. The mechanisms and components of the HP1 model which are appropriate for this study are described precisely in Jacques and Šimůnek (2005). The form of the one-dimensional Richards equation for variably-saturated water flow and advection-dispersion type equations for heat and solute transport is solved numerically by the Garlerkin-type linear finite element approach, which assumes that the air phase plays an insignificant role in the liquid flow process and that water flow due to thermal gradients can be neglected (Šimůnek et al., 2013). The dual porosity van Genuchten-Mualem model was used in this study because of comparison with results from soil packed into a long column (400 mm height, and 87.5 mm diameter) and the experimentation period. Differences in pH, cation-exchange capacity, organic matter, and clay particle thickness can possibly tend to explain the different compaction behaviours and soil water retention (Assouline et al., 1997). Thus, the measured saturated and residual water content prior to and after experimentation with optimised α and n parameters were used for the HYDRUS-1D modelling (Table 6.3). At the end of experimentation, soil columns were dismantled and samples collected from 5, 15, 25 and 35 cm depths to determine residual and saturated water content, bulk density as well as saturated hydraulic conductivity K_s. The effects of soil packing and chemistry of the applied solutions on soil compaction and saturated hydraulic conductivity were observed in particular for Dalby and Eldorado soils, while the Maryborough soil columns presented insignificant differences in bulk densities. Jacques et al. (2002) indicated that lower hydraulic conductivity is needed for the calibration of water and solute transport in the lower depths of the soil profile. Therefore, the bulk density and K_s of layers in simulated soil profiles were matched to the experimental data.

To simulate water movement, the initial and boundary conditions used for HYDRUS-1D were established to match the laboratory experimentation. A variable pressure head boundary condition was applied at the top and free drainage at the lower boundary condition. The concentration boundary condition was selected upper as a Cauchy-type boundary condition. This ensures that the concentration of applied solution at the top of soil profile depends on the concentration of ions in the solution that was applied (Leij et al., 1991; Reading et al., 2012). For the lower boundary condition, the "zero gradient boundary condition" is most appropriate for semi-infinite and infinite systems in that it assumes the concentration is continuous across the lower boundary and specifically when the flow is directed out of the modelled domain (Leij et al., 1991; Šimůnek et al., 2013). The initial pressure head of the soils was set depending on the soil. The model's temporal and spatial discretization schemes were estimated by the Galerkin finite elements and Crank–Nicholson Scheme as described by (Šimůnek et al., 2013). A coarse grid spacing of 2 cm was used previously for HYDRUS-1D simulations (Šimůnek & Suarez, 1997), but a finer grid spacing of 1 cm was used in this case as it was more appropriate for 40 cm soil depth used. The exchangeable cations used as initial parameters in the simulations were the composition of each exchange component equilibrated with soluble ions specified for each depth. The aqueous phase was able to react with the assemblage of solid phases reversibly such as sulphur compounds for acidic soil and calcite ($CaCO_3$) for alkaline soil.

At the beginning of experimentation, soil columns received 0.7 pore volume of each typical applied solution, and then the soil solution was sampled using microfiber tubes (Figure 6.1), and the solute compositions were set as the initial soil solution for each depth. The composition of the applied solution and the soil chemical and hydraulic properties used in the simulations are shown in Table 6.2 and 6.3.

Since the HP1 module in the HYDRUS model does not predict the hydraulic conductivity reduction, the HYDRUS model was re-run using the major ion chemistry module, and hydraulic conductivity reduction function activated using the same scenarios applied to the HP1 module. The major ion chemistry module in HYDRUS is considered to be useful for modelling agricultural scenarios because the impacts of precipitation, salt accumulation, dissolution of common minerals, cation exchange, irrigation and evapotranspiration (Reading et al., 2012; Šimůnek et al., 1998) which is expected to cause soil structural degradation and hydraulic reduction.

Table 6.3 The HYDRUS model inputs used.

Parameter	***Soil 1***	***Soil 2***	***Soil 3***
	Mean values		
Number of soil material	1	1	1
Number of layers for mass balance	4	4	4
Depth of soil profile (cm)	40	40	40
Exchangeable cations ($\mathrm{cmol_c\ kg^{-1}}$)			
Ca	0.349‡	12.43‡	9.99‡
Mg	0.899‡	8.32‡	1.52‡
Na	0.058‡	1.83‡	2.7‡
K	0.056‡	0.61‡	1.19‡
Fe	0.14‡	0.0033‡	0.01‡
Al	0.314‡	0.001‡	0.003‡
Cation exchange capacity ($\mathrm{cmolc\ kg^{-1}}$)	1.81‡	23.2‡	15.41‡
Bulk density ($\mathrm{g\ cm^{-3}}$)	1.26‡	1.25‡	1.29‡
Diffusion coefficient ($\mathrm{cm^2\ min^{-1}}$)	0.001	0.0014	0.0013
Dispersivity (cm)	1	1	1
$K_{Ca/Mg}$	0.445‡	1.12‡	3.07‡
$K_{Ca/Na}$	0.413‡	2.9‡	8.7‡
$K_{Ca/K}$	0.438‡	1.36‡	1.15‡
Hydraulic model	Van Genuchten- Mualem		
Residual water content (θ_r)	0.0117‡	0.0389‡	0.0356‡
Saturated water content (θ_s)	0.364‡	0.5‡	0.482‡
Saturated hydraulic conductivity ($\mathrm{cm\ day^{-1}}$)	20.16‡	8.6‡	6.94‡
Inverse of the air entry suction (α) ($\mathrm{cm^{-1}}$)	0.037†	0.02†	0.021†
Pore size distribution, n	1.25†	1.145†	1.17†
Tortuosity pore connectivity parameter (l)	0.5†	0.5†	0.5†
Grid spacing (cm)	1	1	1
Initial time step (day)	0.001	0.001	0.001
Min. time step (day)	$1\mathrm{x}10^{-5}$	$1\mathrm{x}10^{-5}$	$1\mathrm{x}10^{-5}$
Max. time step (day)	290	290	290

‡ Measured properties for the soils used in laboratory experiments.
† Optimised properties using inverse modelling (Rosetta)

6.2.7. Statistical analysis

The observed and predicted results were analysed using a calculated Pearson's product-moment correlation coefficient. The mean absolute deviation (MAD; Equation 6.14) (Huber, 2011), mean absolute percentage error (MAPE; Equation 6.15) (Armstrong & Collopy, 1992), root mean square error (RMSE; Equation 6.16) (Willmott & Matsuura, 2005), index of agreement (I_A; Equation 6.17) (Willmott, 1981), the coefficient of determination (R^2; Equation 6.18) where predicted values fitted to y=x line as well as average Euclidean distance (AED) from the line y=x were used to assess the level of agreement between the observed and predicted results to validate the model.

$$MAD = \frac{\sum_{i=1}^{n}|P_i - O_i|}{n}$$ **Equation 6.14**

$$MAPE = \left(\frac{1}{n}\sum_{i=1}^{n}\frac{|P_i - O_i|}{O_i}\right) \times 100$$ **Equation 6.15**

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}|P_i - O_i|^2}{n}}$$ **Equation 6.16**

$$I_A = \frac{\sum_{i=1}^{n}(P_i - O_i)^2}{\sum_{i=1}^{n}(|P_i - \bar{O}| + |Oi - \bar{O}|)^2}$$ **Equation 6.17**

$$R^2 = 1 - \left(\frac{\sum_{i=1}^{n}(P_i - O_i)^2}{\sum_{i=1}^{n}(P_i - \bar{P})^2}\right)$$ **Equation 6.18**

where, P_i is the predicted value, O_i is observed value, $\overline{P}$ and $\overline{O}$ are the mean value of predicted and observed values, respectively. The lower the MAD, MAPE and RMSE values the better the predictive capability of a model in terms of its absolute deviation. The values of R^2 and I_A ranges from zero to 1.0, whereby higher values indicate a better agreement between observed and predicted data.

6.3. Results

6.3.1. Hydraulic conductivity reduction due to alkalinity

The simulations of the HP1 module assumed that irrigation water chemistry does not affect the hydraulic conductivity dynamic. In general, the major ion chemistry module with the selected K_{red} function was able to simulate the effect of soil solution chemistry on K_{red}. The HYDRUS model, however, was able to simulate K, with an R^2=0.39 between observed and simulated results (for the current HYDRUS K-pH-dependent model) for all soils and treatments. The observed K was calculated from the K_s results of soils after soil column dismantlement using Equation 6.3 (Van Genuchten, 1980). For all soils and reduction functions, the observed and predicted results showed that there was a progressive increase in K reduction with increasing alkalinity of irrigation water. The magnitude of this decrease, in comparison to the control, was significant due to the alkalinity concentration, and evident for both the observed and predicted results.

A generalised and non-linear function (Equation 6.7 and 6.8) were compared to the HYDRUS standard pH driven reduction function in order to determine the magnitude of improvement the new models provided. Statistical parameters for these observed versus predicted values indicated that there was a higher correlation obtained for both the new generalised (Equation 6.7) and non-linear (Equation 6.8) models in comparison to the current HYDRUS K-pH-dependent function (Figure 6.3). Accordingly, statistics demonstrated a significant improvement (P_{value}<0.001) in the predicted K for these new generalised and non-linear equations.

Figure 6.3 demonstrates that the K data are consistently better predicted using the new non-linear equation, although the new generalised linear equation performs reasonably well in comparison to the current HYDRUS K-pH-dependent function. The performance of the non-linear equation suggests that soil-specific attributes will be important in explaining the reduction in hydraulic dynamics. This result is expected to occur, given the literature indicating that soil hydraulic conductivity reduction is highly soil-specific (Bennett et al., 2019a; Marchuk & Rengasamy, 2012; McNeal & Coleman, 1966).

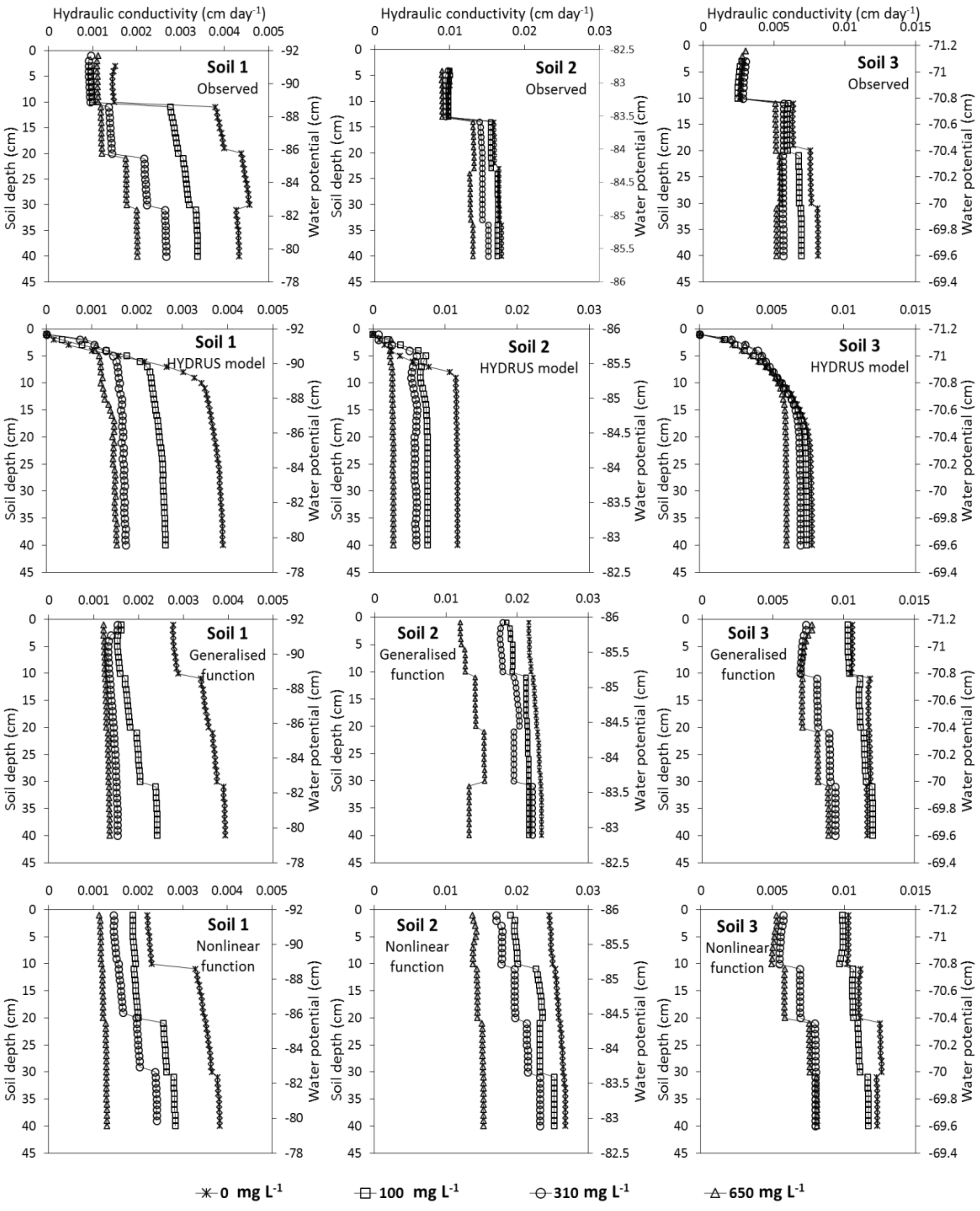

Figure 6.2 The observed and predicted hydraulic conductivity (*K*) (cm day^{-1}) under an unsaturated condition for soils treated with the alkalinity of 0, 100, 310 and 650 mg L^{-1} after 290 days. The saturated hydraulic conductivity (K_s) was measured at the end of the experiment and converted to unsaturated hydraulic conductivity (*K*) using the method of Van Genuchten (1980) (Equation 6.3).

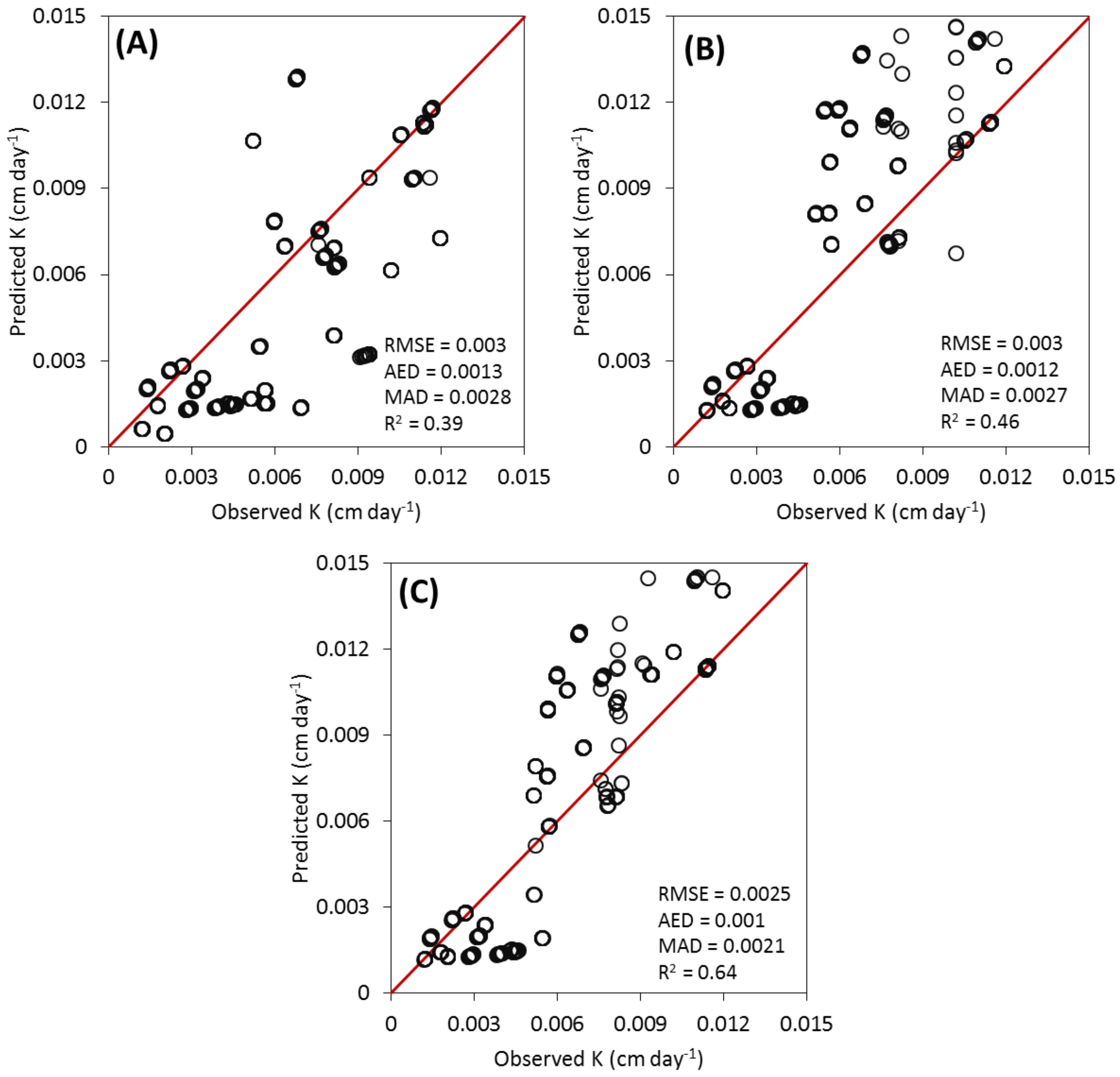

Figure 6.3 The observed and predicted hydraulic conductivity (cm day^{-1}) under unsaturated condition for soils treated with the alkalinity of 0, 100, 310 and 650 mg L^{-1} after 290 days using A) the current HYDRUS K-pH-dependent model, B) the new generalised model, and C) the non-linear function. The Saturated hydraulic conductivity was measured after the experiment and converted to unsaturated hydraulic conductivity using the method of Van Genuchten (1980) (Equation 6.3). RMSE is the root mean square error, AED is average Euclidean distance from the line y=x, and MAD is the mean absolute deviation.

6.3.2. Changes in soil salinity and sodicity due to alkalinity

Irrigation with the alkaline irrigation waters had no significant effect ($P>0.05$) on soil salinity (Figure 6.4, 6.8 and 6.12) because the experimental design allowed for adequate leaching to occur. In addition, the use of irrigation waters with a low ionic composition (2.1 dS m^{-1}; Table 6.2) did not cause salinization. The initial salinity of the deeper layers gradually decreased during experimentation, often reaching the salinity of the applied irrigation water (2.0 ±0.4 dS m^{-1}), depending on the soil and applied alkaline solutions. A slight decrease in salinity was observed for the soils treated with high alkalinity solutions in comparison to non-alkaline solutions. In general, Soil 2 and Soil 3 maintained higher salinity than Soil 1, which was expected, due to greater CEC of soils 2 and 3, these two soils having less leaching for the same irrigation volume, due to higher clay content. The changes in the soil sodium adsorption ratio (SAR) under different alkalinity application treatments are shown in Figure 6.5, 6.9 and 6.13. The soil solution SAR of all soils gradually increased with time as the alkalinity of the applied solution increased. In general, the HYDRUS simulation slightly underestimated salinity and sodicity for the experimentation period, excluding the initial sampling time, as this point in time was an input into the model.

The salinity and sodicity prediction were totally dependent on the initial input values which caused different salinity and sodicity in a specific soil treated with different levels of alkalinity. Common to all soils, the soil SAR values was greater when treated with greater alkaline concentration than when treated with zero or low alkaline solutions for observed and HYDRUS predicted results. The observed and predicted results depicted that the increase in solution SAR was the highest (SAR$\approx$ 23) for the acidic soil (Soil 1) due to increasing alkalinity, especially HCO_3^-=650 mg L^{-1}, while this trend was less evident for neutral and alkaline soils. Moreover, the increase of SAR was the highest for the upper layers (0–15 cm depth) than deeper in the columns for all treated soils. The overall statistical parameters (MAPE, RMSE, I_A and R^2) for EC and SAR values indicate that the predicted results are in relatively good agreement with observed results for all soils (Figure 6.16).

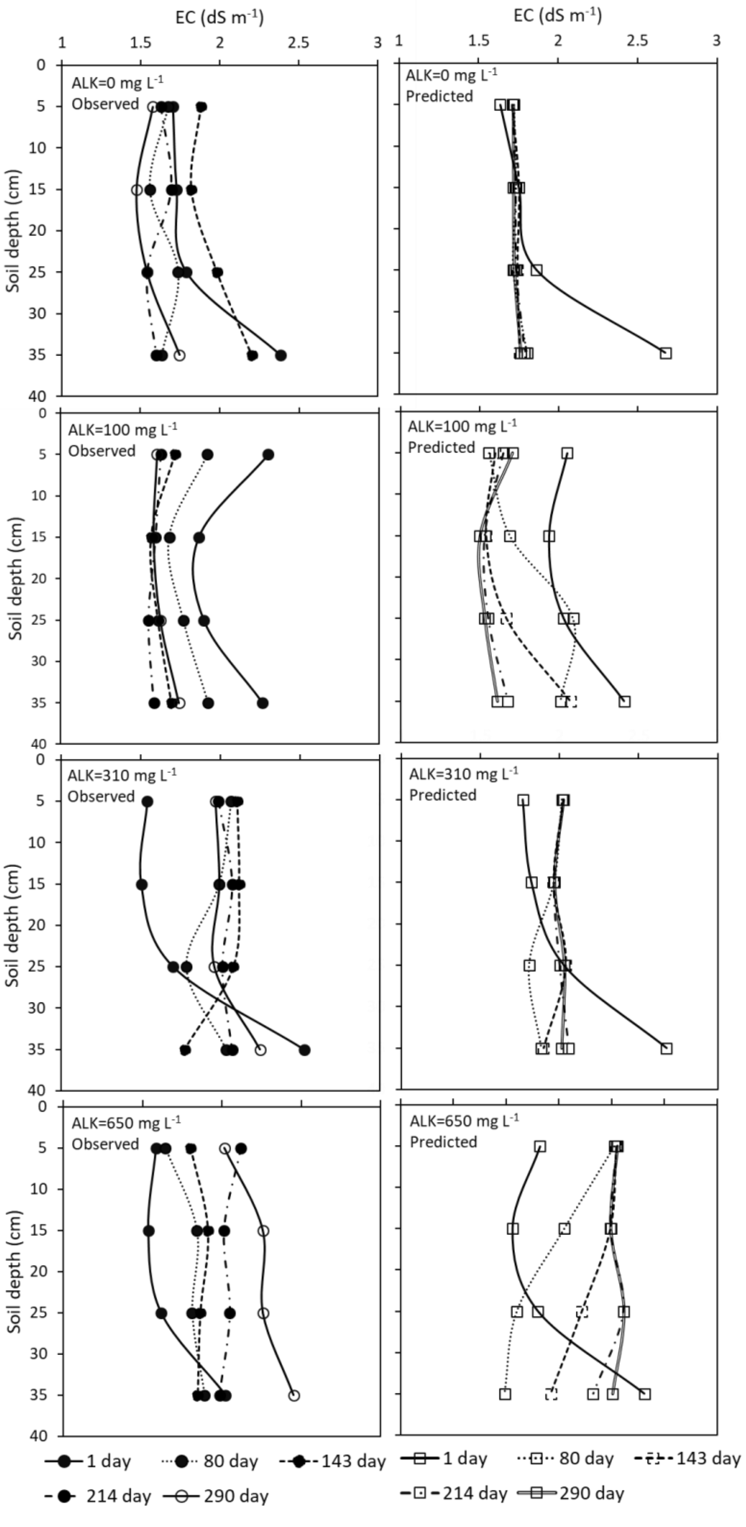

Figure 6.4 The observed and HYDRUS model results of electrical conductivity (dS m^{-1}) of the extracted solution at depth 5, 15, 25 and 35 cm for Soil 1.

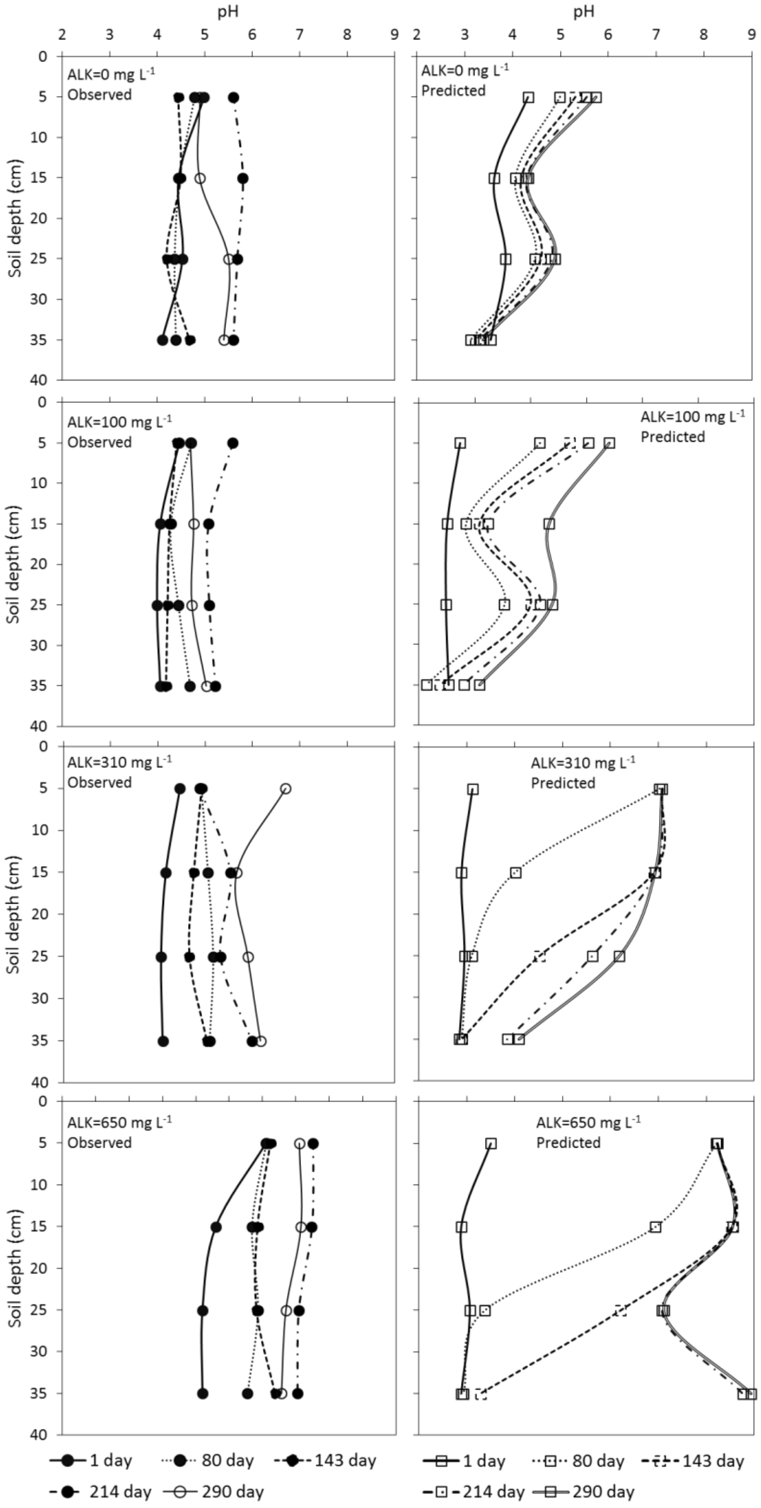

Figure 6.5 The observed and HYDRUS model results of sodium adsorption ratio (mmol$_c$ L^{-1})$^{0.5}$ of the extracted solution at depth 5, 15, 25 and 35 cm for Soil 1.

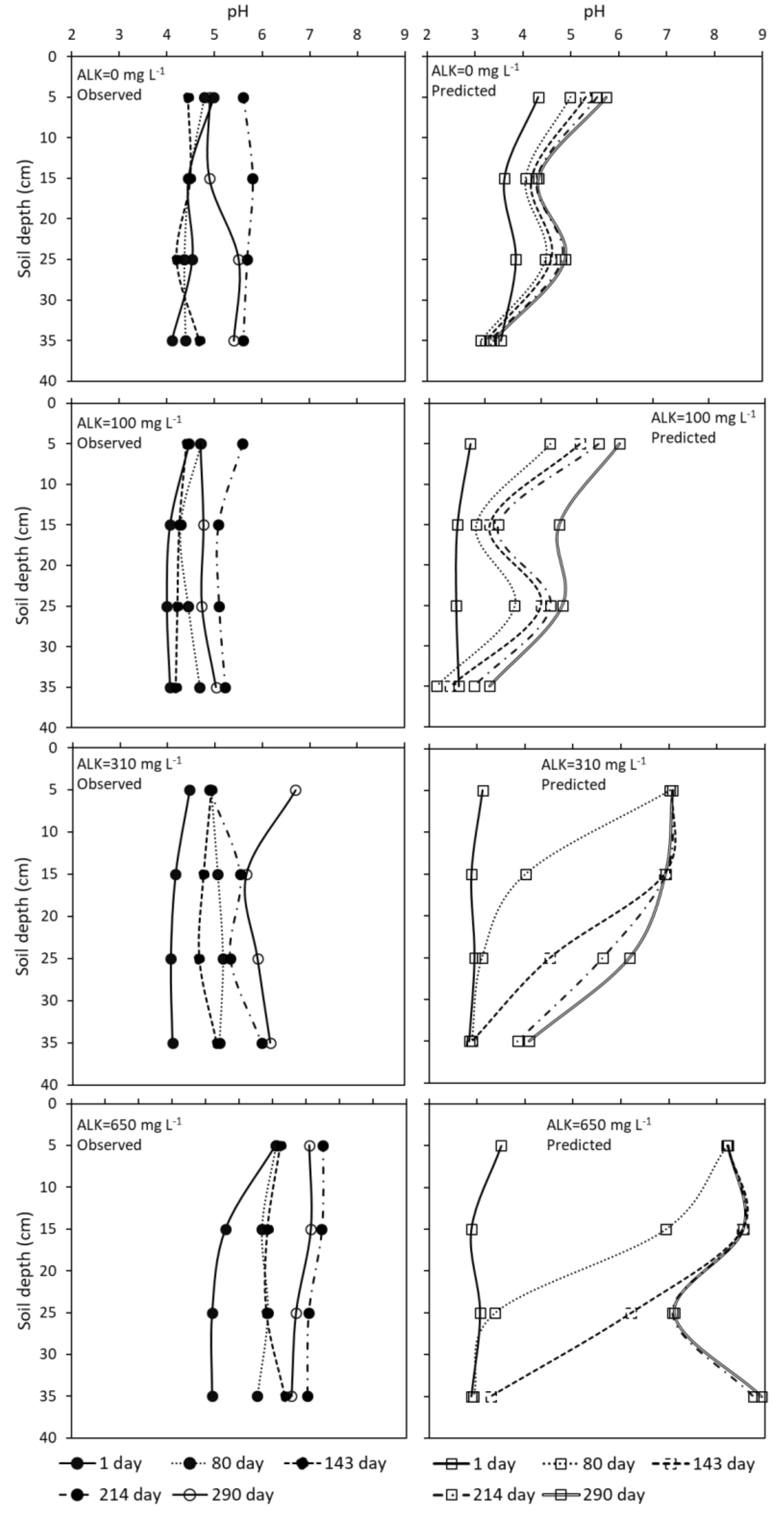

Figure 6.6 The observed and HYDRUS results of pH of the extracted soil solution at depth 5, 15, 25 and 35 cm for up to 290 days period for Soil 1.

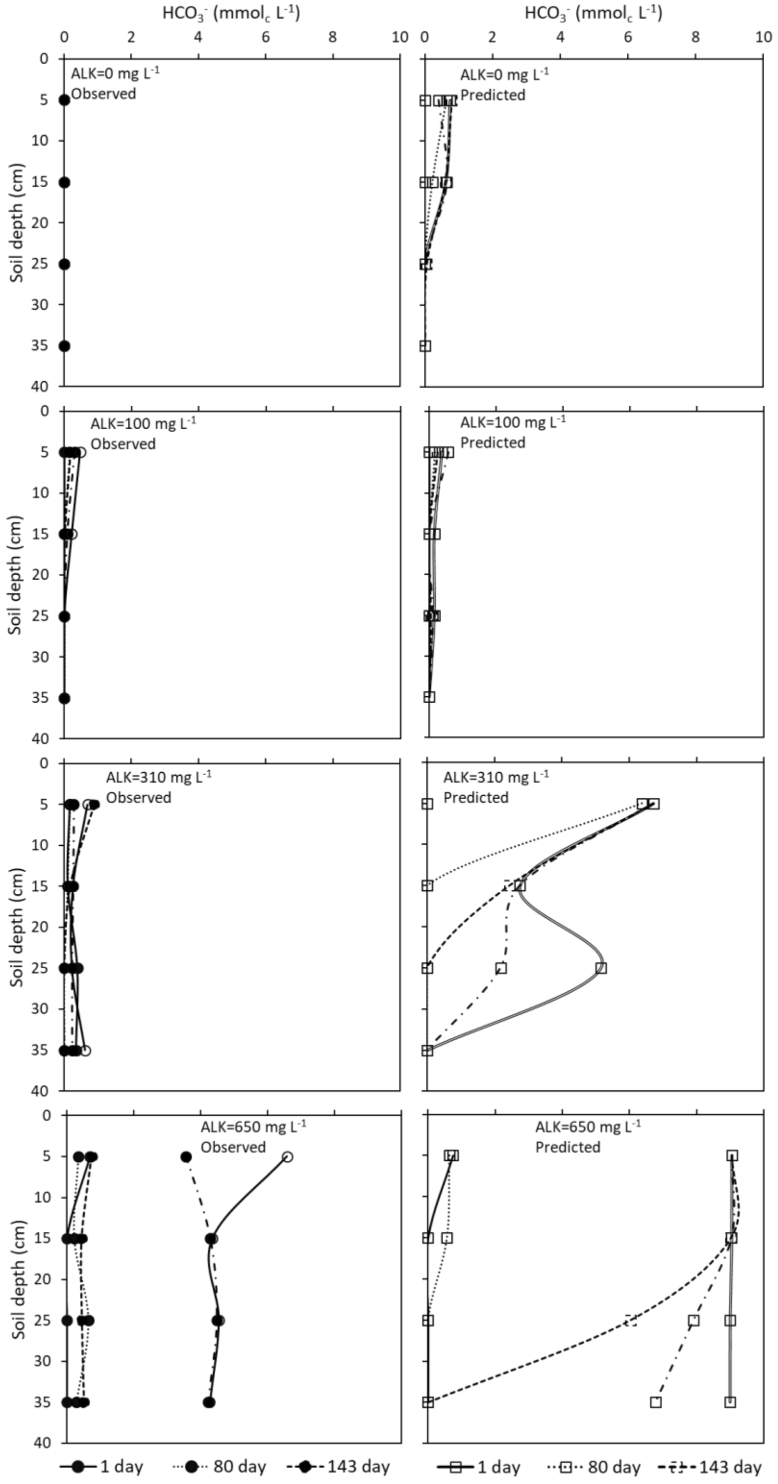

Figure 6.7 The observed and HYDRUS results of alkalinity (HCO$_3^-$) of the extracted soil solution at depth 5, 15, 25 and 35 cm for up to 290 days period for Soil 1.

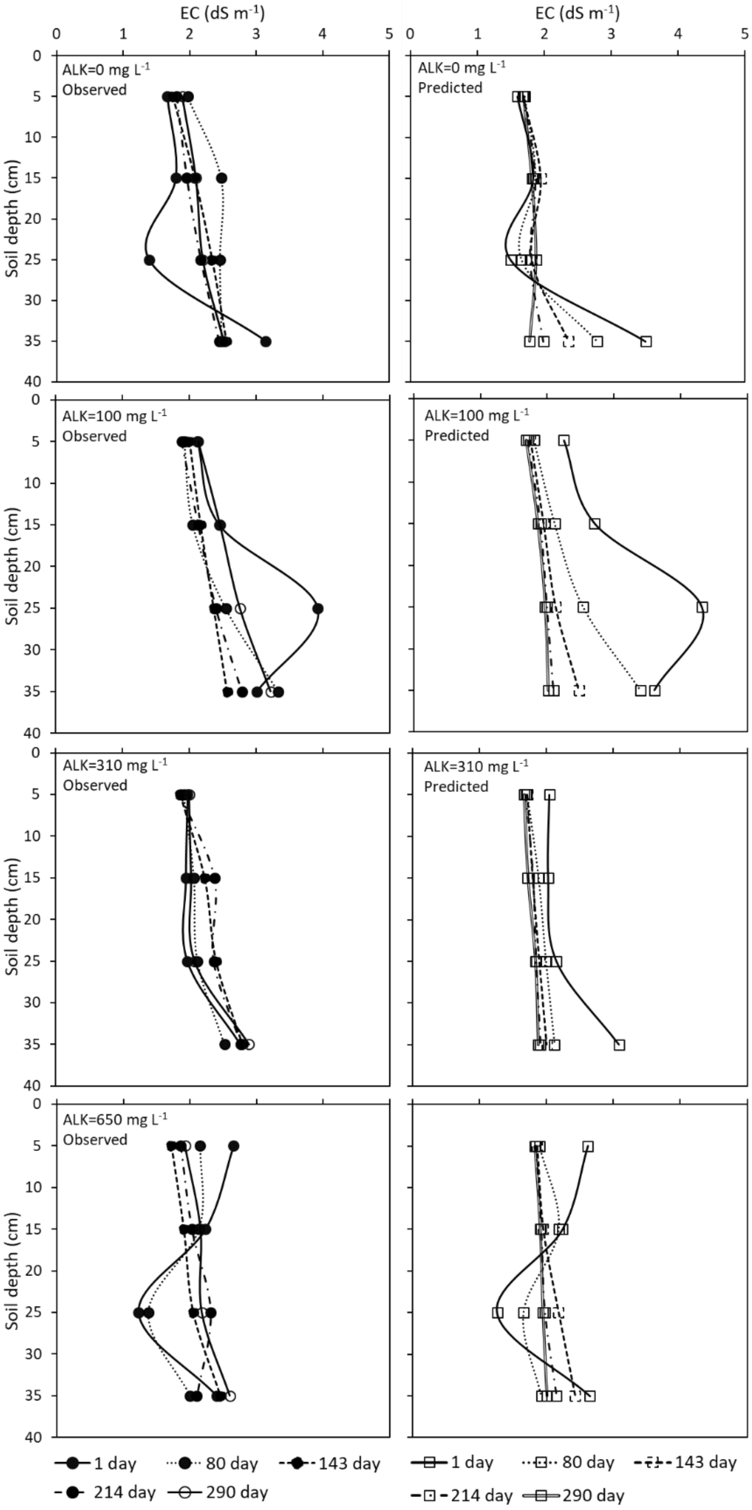

Figure 6.8 The observed and HYDRUS model results of electrical conductivity (dS m^{-1}) of the extracted solution at depth 5, 15, 25 and 35 cm for Soil 2.

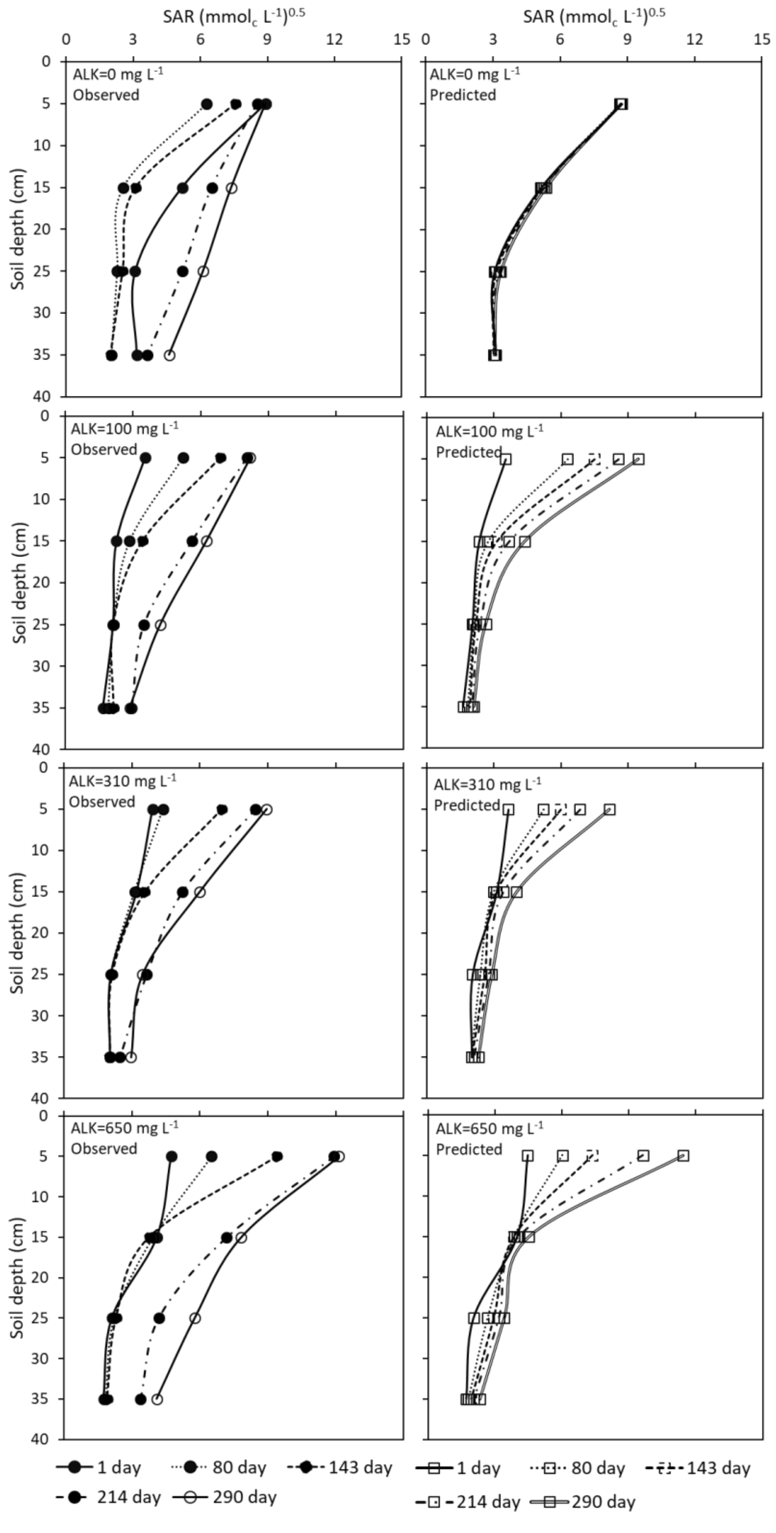

Figure 6.9 The observed and HYDRUS model results of sodium adsorption ratio (mmol$_c$ L^{-1})$^{0.5}$ of the extracted solution at depth 5, 15, 25 and 35 cm for Soil 2.

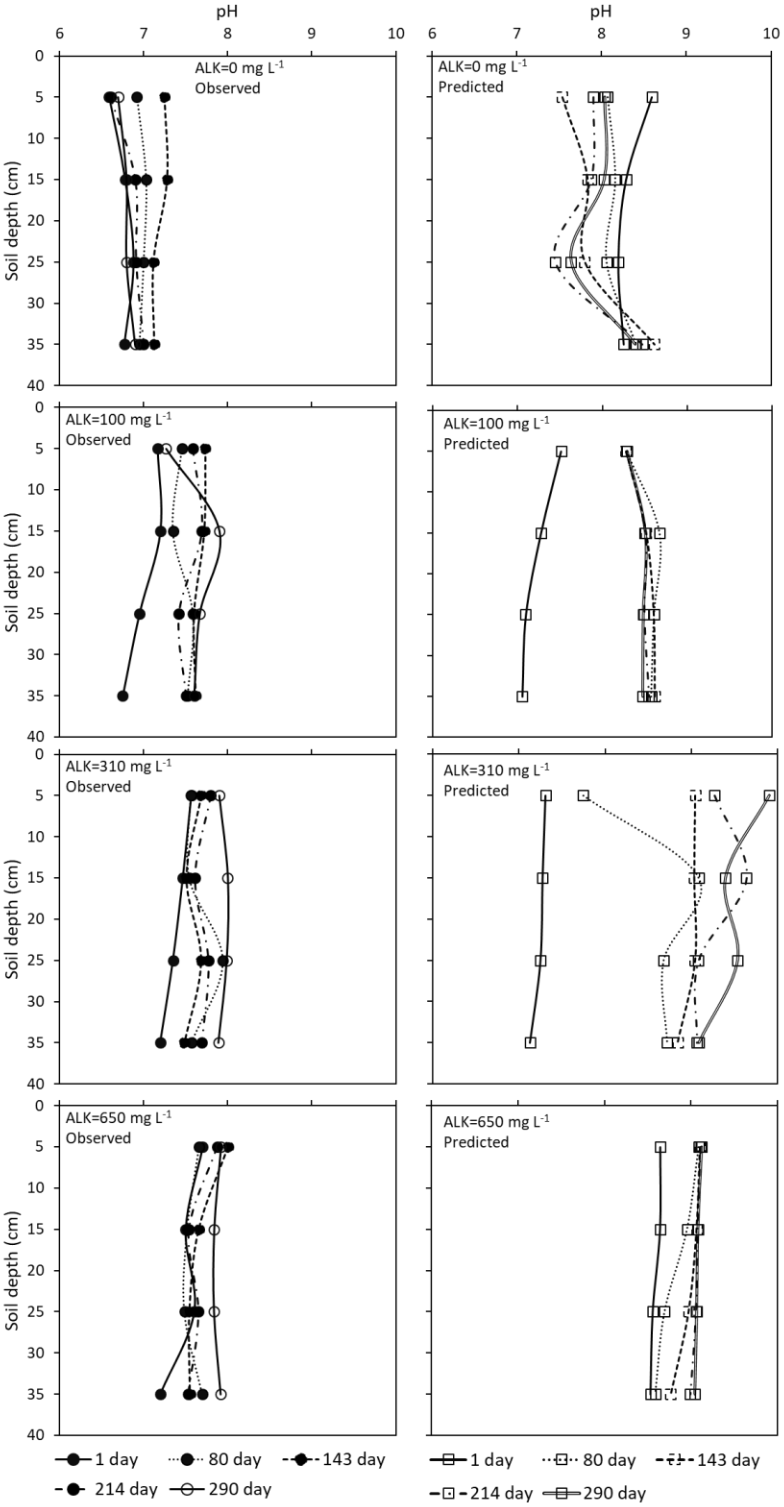

Figure 6.10 The observed and HYDRUS results of pH of the extracted soil solution at depth 5, 15, 25 and 35 cm for up to 290 days period for Soil 2.

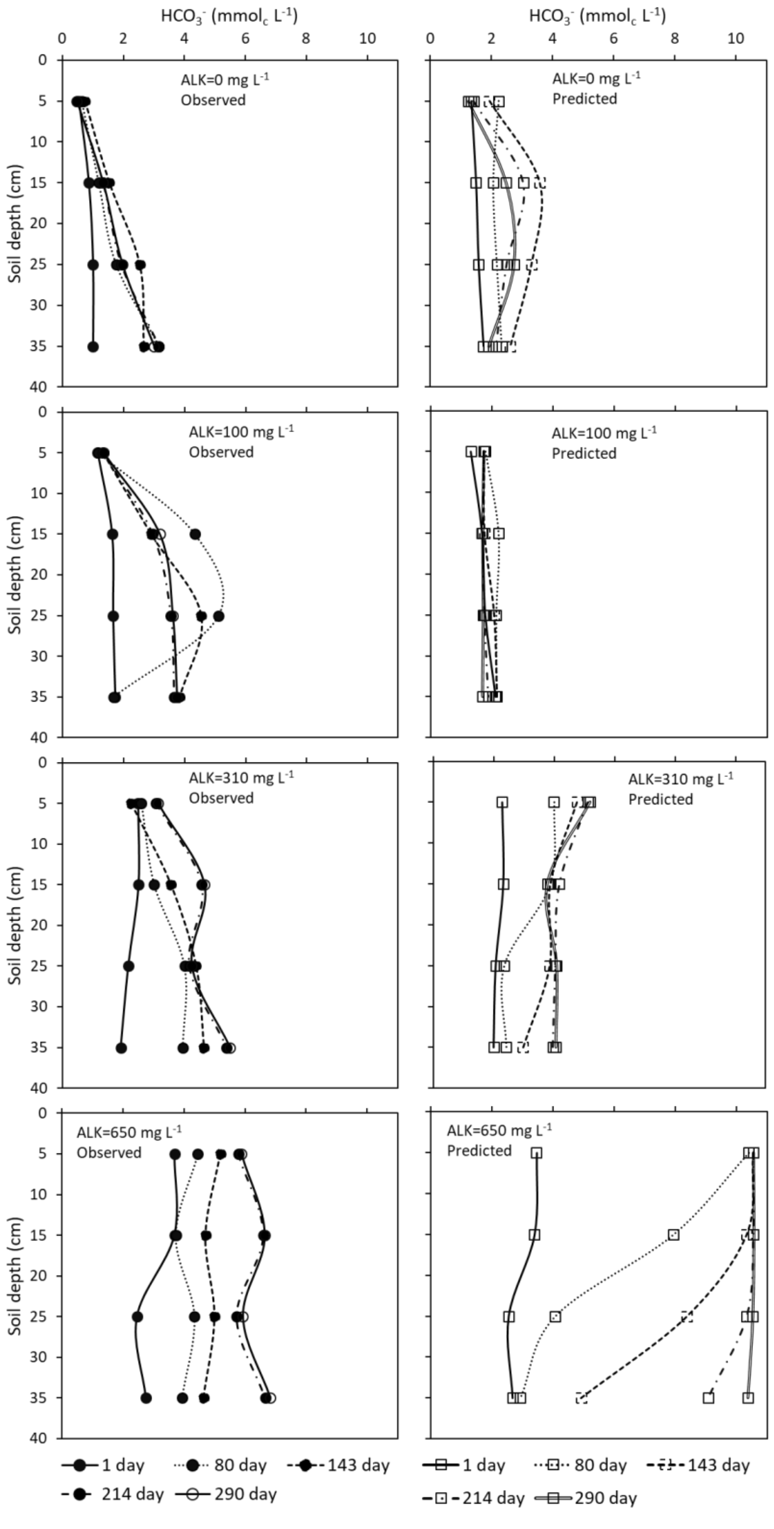

Figure 6.11 The observed and HYDRUS results of alkalinity (HCO_3^-) of the extracted soil solution at depth 5, 15, 25 and 35 cm for up to 290 days period for Soil 2.

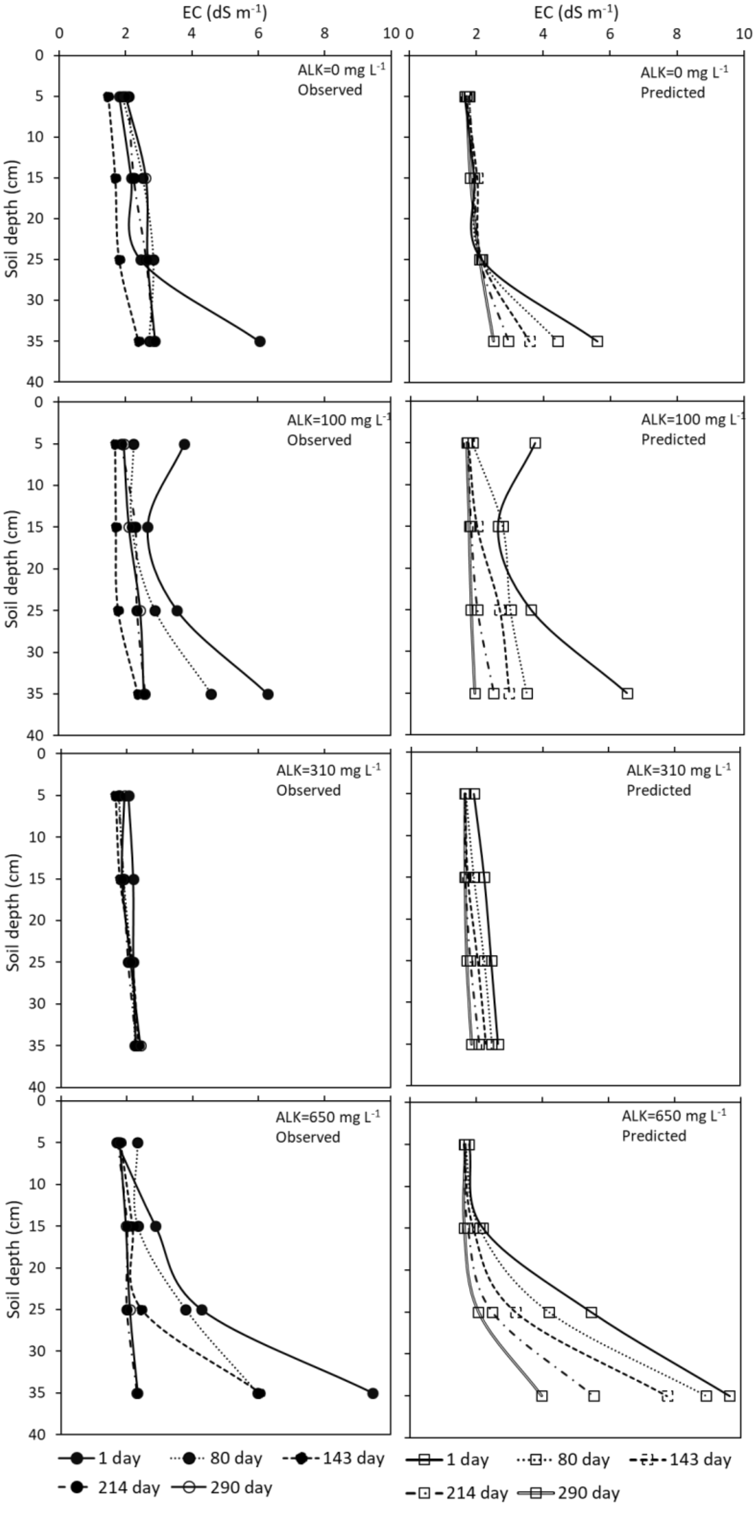

Figure 6.12 The observed and HYDRUS model results of electrical conductivity (dS m^{-1}) of the extracted solution at depth 5, 15, 25 and 35 cm for Soil 3.

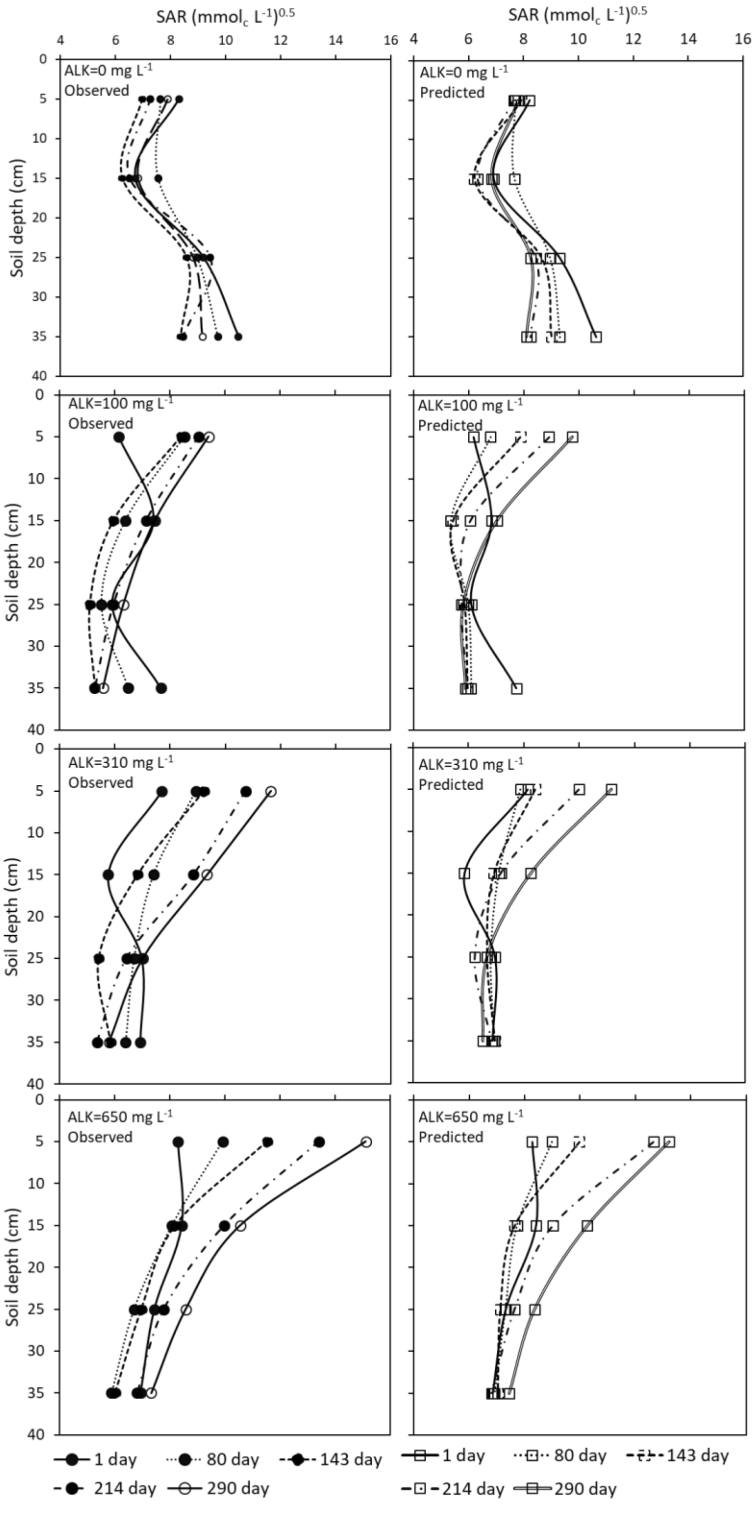

Figure 6.13 The observed and HYDRUS model results of sodium adsorption ratio (mmol$_c$ L^{-1})$^{0.5}$ of the extracted soil solution at depth 5, 15, 25 and 35 cm for Soil 3.

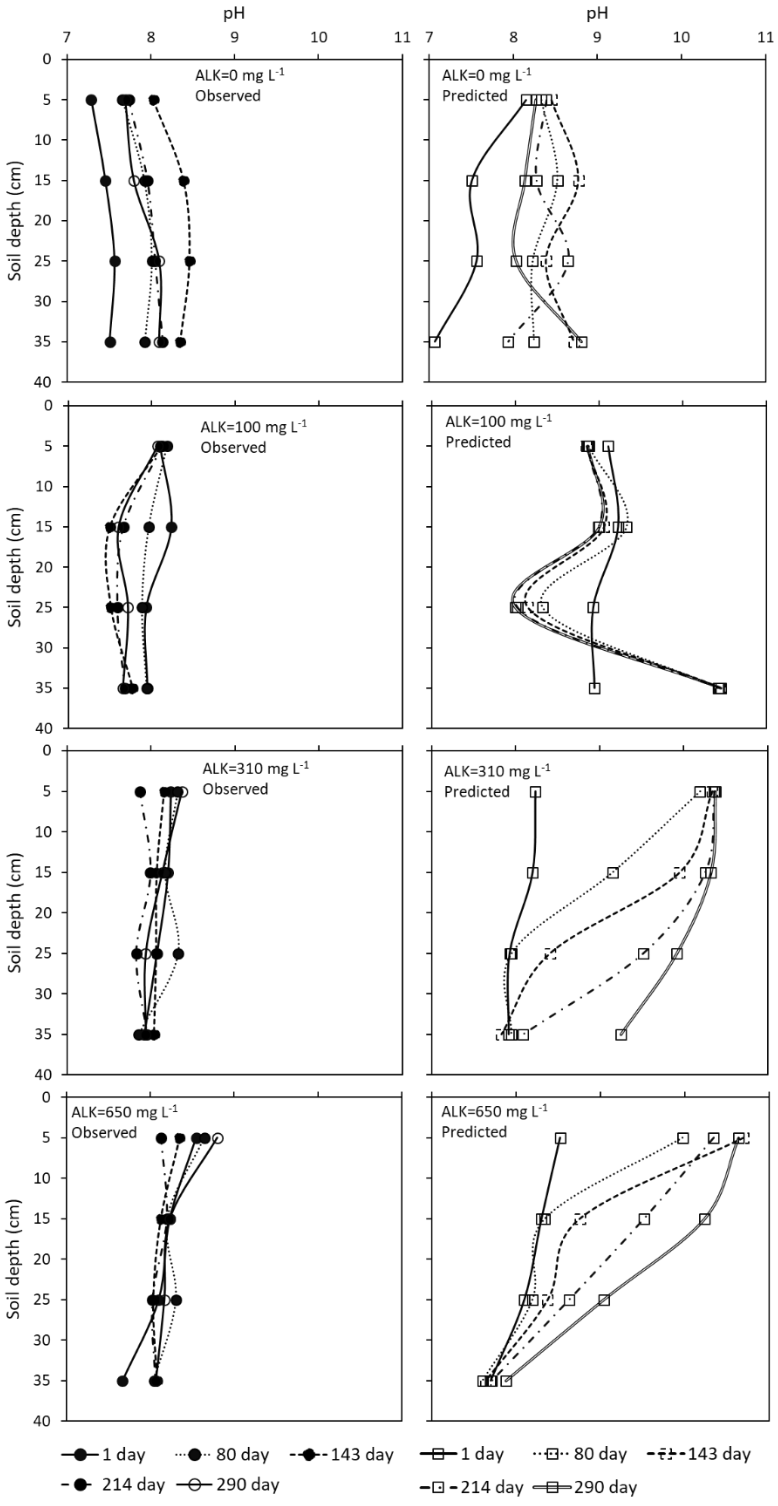

Figure 6.14 The observed and HYDRUS results of pH the extracted soil solution at depth 5, 15, 25 and 35 cm for up to 290 days period for Soil 3.

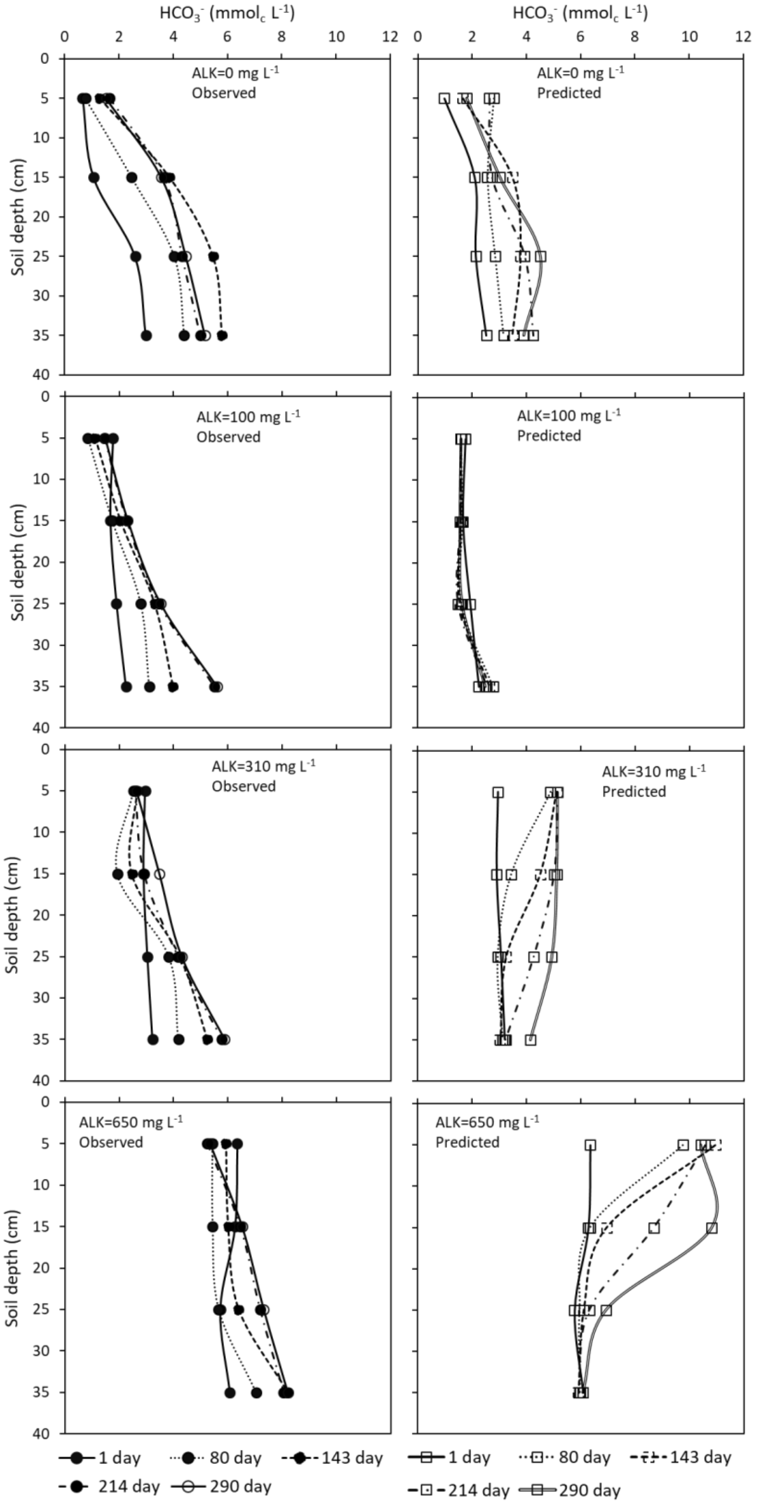

Figure 6.15 The observed and HYDRUS results of alkalinity (HCO$_3^-$) of the extracted soil solution at depth 5, 15, 25 and 35 cm for up to 290 days period for Soil 3.

6.3.3. Changes in soil pH and alkalinity due to the alkalinity of irrigation water

The soil solution pH and alkalinity (HCO_3^-) progressively increased as the leaching time increased in all soils treated with alkaline solutions. Solution pH and alkalinity concentration increased in the 0–25 cm depth under alkaline irrigation water (Figure 6.6, 6.7, 6.10, 6.11, 6.14 and 6.15) leading to an increase in solution SAR (Figure 6.5, 6.9 and 6.13). Additionally, the increase in alkalinity was greater for the originally alkaline (Soil 3) and neutral (Soil 2) soils, due to excess build-up of alkalinity in the soil system, which would be expected.

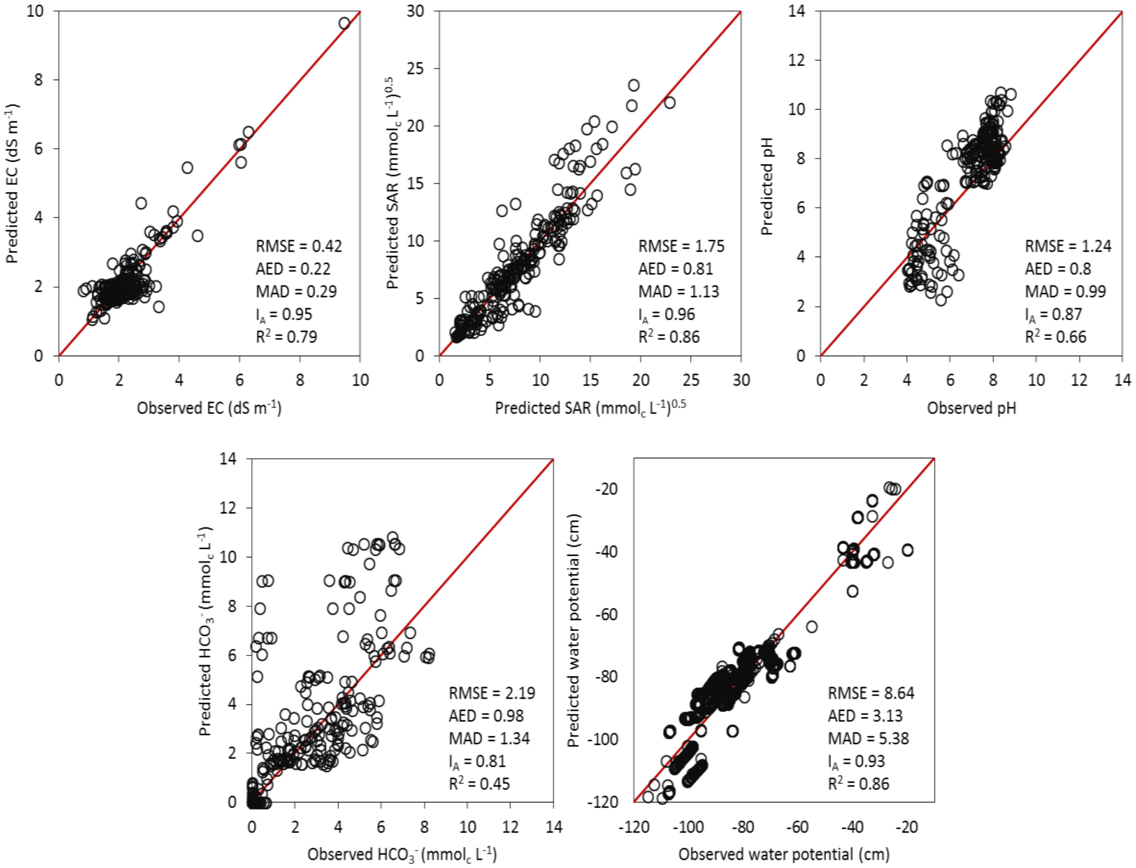

Figure 6.16 The relationship between observed and HYDRUS predicted results of electrical conductivity (EC), sodium adsorption ratio (SAR), pH, alkalinity (HCO_3^-) and water potential. The diagonal red line represents the y=x line. RMSE is the root mean square error, AED is Average Euclidean Distance from the line y=x, MAD is the mean absolute deviation, and I_A is the index of agreement (Willmott, 1981).

However, the simulated results from the HYDRUS model generally predicted a greater increase in pH and alkalinity for all soils, increasing as irrigation alkalinity increased. This resulted in a lower agreement between the observed and predicted results for pH and alkalinity, than for the other measured chemical characteristics. The exceptions were soils treated with non-alkaline and low level alkalinity (100 mg L^{-1}) irrigation water, where the observed pH and alkalinity were higher than the predicted pH and alkalinity of the HYDRUS model. The overall statistical parameters (AED and RMSE) for pH and HCO_3^- values indicate that the predicted results are in relatively poor agreement with observed results for all soils with having RMSE of 1.24 and 2.19 for pH and HCO_3^-, respectively (Figure 6.16).

6.4. Discussion

6.4.1. Hydraulic conductivity prediction

The developed generalised and non-linear models of Ali et al. (2019b) performed significantly better than the current HYDRUS K-pH-dependant function for hydraulic conductivity change prediction. Specifically, there was a greater agreement between observed and predicted *K* values for the non-linear function. The simulation results of the current HYDRUS K-pH-dependant function was in the least agreement with observed *K* results, especially for a neutral and high clay content, vertic soil (Soil 2). The latter soil showed higher resiliency in terms of increasing alkalinity within the solution and this effect was significantly underestimated in the HYDRUS model using the standard reduction function. The current optimum condition for solution pH is 6.83 in the standard HYDRUS K_{red} model, which implies the pH has zero effect on K_{red}≤6.83. A recent study of Ali et al. (2019a) confirmed that this effect is dependent on clay content, initial soil pH and ionic strength (Equation 6.8). The better performance of the non-linear function (pedotransfer function) should be expected, due to including factors responsible for *K* reduction, thus allowing a soil-specific response. However, there was 36% remaining variation unexplained by the model prediction factors, which is most likely a function of HYDRUS treating the concentration and pH scaling factors as independent, as well as factors such as clay mineral suite (e.g. surface charge and size) and organic matter which are not captured within the model, due to insufficient data to incorporate them. In spite of the fact that the non-linear model should undergo future development as data becomes available, the results of hydraulic conductivity prediction by the generalised and non-linear functions of Ali et al. (2019b) showed better K_s prediction (Figure 6.3). It should be noted that the improved generalised function still performs relatively poorly, with 54% of variation unexplained by the prediction function, leading us to accept that the non-linear function is the more acceptable approach.

This experiment utilised gently crushed, sieved and repacked soil in long columns within a laboratory environment, which might be suggested to not represent effects in the field because of the loss of antecedent soil structure, pore network disturbance, reliance on chemical equilibrium and differing climate conditions between laboratory and field conditions. However, the importance of the work is that provides validation against reduction mechanisms that would be expected to operate similarly within the field condition where pore continuity and pore size frequency are expected to be different. That is, the mechanistic change in clay swelling, disaggregation and dispersion with the change in the solute suite are transferable to the field, but the absolute values would likely not be. The soil columns were subjected to unsaturated conditions and multiple cycles of wetting and drying in the presence of alkaline water throughout an experimental duration of 290 days. On this basis, we suggest that the modelling results are an acceptable validation when considering the need to control for complex processes, including the equilibrium chemical reactions between components such as complexation, cation adsorption-exchange and precipitation-dissolution, the change in exchangeable sodium, and change in pH of the soil solution. Future work should make assessments in the field, but this is a valuable first step. Therefore, we suggest that the non-linear function (Equation 6.8) replace the current r_2 scaling factor in the HYDRUS-1D model in order to improve HYDRUS as a predictive tool for solute movement, chemical equilibria dynamics and hydraulic dynamic changes in the soil profile under alkaline irrigation water application in variably saturated regimes.

6.4.2. Land response to alkaline irrigation is soil-specific

Our findings demonstrated that the degradative effect of increasing alkalinity was different for each of the soils, depending on the level of alkalinity of irrigation water and ionic strength. This confirms the fact that soils have a specific response to the alkaline irrigation water. The soil-specific response is postulated to be due to heterogeneity of soils in clay content, mineralogy, oxide components, organic matter content and clay platelet-specific surface area characteristics (Ali et al., 2019a; Bennett et al., 2019a; Chorom & Rengasamy, 1997; Goldberg et al., 1990; McDowell, 2003; Murray & Quirk, 1990; Sumner et al., 1991). The studies referenced found that the above soil parameters are the major factors governing soil structural stability, and the current study supports these finding within the specific context of alkaline irrigation water. Therefore, the implication is that the suitability of marginal saline-sodic and alkaline irrigation water will be soil-specific, demanding not only land amendment that addresses the water quality but further considers the initial soil properties and legacy management. Treatment of the irrigation solution could be through land application of acidifying materials (Bennett et al., 2016b; McKenna et al., 2019), although there appears to be a paucity of information concerning the background requirement in terms of alkalinity, buffering and the prescribed amendment. Given the soil-specific results in this work without treatment, it is apparent that future work should consider the requirement for calculating combined irrigation and soil amendment strategies.

6.4.3. Mechanisms of hydraulic reduction

Soil columns receiving alkaline irrigation water for 290 days would be expected to be at risk of increased bulk density from swelling of clay (i.e. Soil 2) and settling upon wetting and drying (Levy et al., 2002; Pires et al., 2007; Sirjacobs et al., 2001). Moreover, for all of the tested soils, clay particles that are dispersed from soil surface layers would be expected to infiltrate further into the soil core with subsequent leaching, leading to accumulation within soil pores that reduces their internal diameter. Bennett and Warren (2015) demonstrated that colloidal particles were capable of highly significant soil pore blockage, even where the diameter of the particles was more than 12 times less than that of the soil pores. Therefore, an increased possibility of restricted water permeability and solute movement occurs where both swelling and lodgement of clay particles can occur (Cook et al., 1994; Levy et al., 2002). The resulting *K* for the investigated soils indicates that the alkalinity increased disaggregation when applied in a partially saturated or unsaturated regime, which is expected to be due to increase in bulk density caused by irrigation solution chemistry and concomitant clay dispersion. In addition, the Vertosol was observed to swell, irrespective of chemistry changes. Application of alkaline solutions significantly declined surface hydraulic conductivity (*K)* (Figure 6.3) for both observed and HYDRUS predicted results. Solid phase precipitation (i.e. carbonates) is another factor that can cause pore blockage, resulting in limitation in hydraulic conductivity. The extent of this degradative effect potentially depends on the initial properties of soils such as acidity and alkalinity and clay content (Ali et al., 2019a; Nyamangara et al., 2007). The findings of our work indicate and confirm that the disposal of alkaline irrigation water (i.e. coal seam gas associated water and other alkaline groundwater such as the Australian Great Artesian Basin) to land must be expected to cause a reduction in permeability, due to clay swelling, disaggregation, and dispersion resulting in the reduction of pore size and soil pore blockage (Bennett et al., 2019a; McNeal & Coleman, 1966; Rengasamy & Marchuk, 2011; Shainberg et al., 1981). On this basis, it is imperative that irrigation guidelines and policy stipulate that alkalinity must be sufficiently reduced prior to land application.

6.4.4. HYDRUS-1D model as a predictive tool for land application of alkaline water

The predicted results of pH and alkalinity using the HYDRUS model were generally in less agreement with measured results of pH and alkalinity, while in good agreement for EC and SAR, which indicates that the relatively poor prediction of hydraulic reduction is driven by the pH based scaling factor. This raises questions about the ability of the model to accurately portray potential environmental harm in the planning phase of irrigation systems using marginal quality alkaline waters and the impact on the responding receiving environments. The simulated hydraulic conductivity by the non-linear function suggests that the generalised functions cannot appropriately serve the actual circumstances in the soil on a sufficient soil-specific basis. Furthermore, the addition of the non-linear scaling function significantly improves prediction of the observed hydraulic reduction under saturated (Ali et al., 2019b) and unsaturated conditions, compared to the standard function and as confirmed in this work. Even still, and as identified above, this investigation utilised reconstituted soil cores, and the sample size only represents three soils. Therefore, while the inclusion of the non-linear function improves the predictive capability, it is prudent to present a caveat that model output may not necessarily be correct in terms of potential environmental degradation unless direct validation has occurred for the soil in question. As far as the authors can determine, the HYDRUS tool is used without providing such caveats around hydraulic reduction, which places too much faith in the pH driven scaling factor correctly representing the physical environment. As identified in Ali et al. (2019b), the two scaling factors (r_1 and r_2) in the HYDRUS reduction model (Equation 6.5 and 6.6), are not independent and should in future be combined. This presents a further limitation where the irrigation solution is saline-sodic and alkaline, which should be considered in the accuracy of hydraulic reduction dynamics for planning purposes.

6.5. Conclusion

In this study, the effects of alkaline irrigation water on solute and water movement were assessed using long columns in the laboratory and using the HYDRUS-1D model under unsaturated conditions. The hydraulic conductivity results indicated that the HYDRUS standard model was able to simulate the dynamic changes of hydraulic conductivity in the treated soils and column depth. Introduction of a non-linear hydraulic reduction scaling function significantly improved prediction of hydraulic reduction. pH and alkalinity (HCO_3^-) were found to be the primary drivers of model variability, indicating the pH scaling factor has a large influence over the hydraulic reduction in the HYDRUS model. Whilst the introduction of the non-linear reduction function significantly improves HYDRUS predictive capacity, there remain caveats in its implementation in terms of pure prediction to inform planning for the application of alkaline waters to land and any potential for potential environmental harm. This will be important for practitioners to note in the preparing of reports for land and water based amendment in the strategic use of marginal alkaline waters.

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7. Incorporating solution alkalinity into a hydraulic reduction model to account for disaggregation and dispersion

Abstract

The use of alkaline and sodic water for irrigation has increased in recent years due to constrained freshwater sources and a rapid increase in industrial by-product wastewater from industries such as coal seam gas and effluent management from other industrial sources. The use of alkaline sodic water can significantly impact soil condition, in particular soil physical properties. The threshold electrolyte concentration (C_{TH}) is generally used to assess soil structural stability when it is subjected to a solution of a given sodium adsorption ratio (SAR) and electrolyte concentration (EC). The current Ezlit et al. (2013) disaggregation model is mainly based on the sodium and calcium system, without considering the adverse effects of alkaline anions (e.g. HCO_3^-) to reduce saturated hydraulic conductivity (K_s). This study aimed to assess the incorporation of HCO_3^- into the semi-empirical disaggregation model approach to determine C_{TH}. The percentage reduction in K_s increased with increasing the alkaline solution and this reduction rate was dependent on soil type. The results indicated that there is a great correlation between the C_{TH} reduction of K_s produced by non-alkaline and alkaline solutions represented as SAR and adjusted SAR (SAR_{adj}) for up to 30% K_s reduction. This association confirms that the effect of SAR and SAR_{adj} on C_{TH} are similar. Therefore, HCO_3^- can be incorporated into the current disaggregation model to determine C_{TH} ($\leq$20% K_s reduction) for alkaline irrigation waters when disposed of on lands.

Keywords: *threshold electrolyte concentration, hydraulic conductivity, alkaline water, sodicity, salinity, wastewater.*

7.1. Introduction

The use of marginal quality water for irrigation is progressively increasing in arid and semi-arid regions throughout the world. The rapid increase in the volume of by-product water from industries such as coal seam gas (CSG) and effluent management, as well as greater competition for fresh water resources, has driven a renewed interest in the use of marginal quality saline-sodic and alkaline industrial water and groundwater (Bennett et al., 2016b; Bennett & Warren, 2015; McKenna et al., 2019). Such industrial water is often alkaline, as well as rich in sodium and chloride, with low calcium, magnesium and sulphate concentrations (Kinnon et al., 2010; Taulis & Milke, 2013). This is not dissimilar to the sodic, alkaline groundwater extracted from many aquifers used for agricultural stock, irrigation and domestic purposes (Biggs et al., 2012). These waters are considered marginal to extremely poor by Australian irrigation guidelines (ANZECC, 2000), with use of such water for irrigated agriculture well understood to create agricultural productivity constraints (Oster & Schroer, 1979; Qadir & Oster, 2004; Raine & Ezlit, 2007).

Increasing the electrolyte concentration of a soil solution is generally agreed to improve the hydraulic conductivity of the soil, as a result of increased osmotic potential minimising electrostatic repulsive forces (Quirk, 2001). The threshold electrolyte concentration (C_{TH}) is an important criterion for the appropriate selection of saline-sodic water to maintain soil permeability (Dang et al., 2018a; Ezlit et al., 2013), although it is not well utilised (Dang et al., 2018b; Dang et al., 2018d), and predominantly based on a sodium-calcium system (Ezlit et al., 2013). Given the highly soil-specific nature of the C_{TH}, quantitative prediction for this effect has not yet been fully established (Bennett et al., 2019a; Mau & Porporato, 2015). Furthermore, the effects of alkalinity have not been involved in the investigation of C_{TH} specificity as a function of K_s reduction.

Alkalinity can intensify the negative impact of high SAR water on soil physical and chemical properties, as a result of the precipitation of carbonates in soils with pH greater than 8.5 (Brady & Weil, 2008). High sodium is usually associated with high carbonate and bicarbonate build up and then high pH (Suarez et al., 1984), as a result of the occurrence of calcium and magnesium carbonate precipitation. Various adjustments for calcium precipitation and changes in sodium adsorption ratio (SAR) have been proposed in the literature (Ayers & Westcot, 1976; Bower et al., 1965; Bower et al., 1968; Lesch & Suarez, 2009; Rayment & Higginson, 1992; Rhoades, 1968, 1982; Suarez, 1981). For high calcium and bicarbonate waters, previous researches recommend the use of adjusted SAR (SAR_{adj}) index rather than the standard SAR. The use of SAR_{adj} accounts to some extent for the alkalinity effect on the cation suite when irrigation with alkaline and sodic water occurs. In this case, sodium becomes a dominant cation in the soil solution, subsequently leading to: chemical instability of the soil; clay swelling; disaggregation and dispersion; soil structure degradation; surface sealing; slumping and soil pore clogging; and hydraulic conductivity reduction (Abrol et al., 1988; Bennett et al., 2019a; Mashhady & Rowell, 1978; McNeal et al., 1968; Raine & Ezlit, 2007; Rengasamy & Olsson, 1993). Permanent (without significant mechanical intervention) reduction in soil infiltration capacity and water availability occurs where soils disperse, which further exacerbates surface runoff, flooding, and soil erosion (Viviani & Iovino, 2004), and results in decreased vegetation productivity (Johnston et al., 2008; So & Aylmore, 1993). Although, these effects are usually attributed to exchangeable sodium concentrations and sodic soils by practitioners, rather than to the potential effects of irrigating a non-sodic soil with an alkaline irrigation source.

The effects of alkalinity and exchangeable sodium percentage (ESP) on the physicochemical properties and crop growth are not easy to separate, because high pH and high ESP often occur together (Marchuk, 2013; Suarez et al., 1984). The HYDRUS model (Šimůnek et al., 2016) uses a scaling factor approach where the pH and SAR components of the model are independent functions, although Ali et al. (2019a) demonstrated for different pH, EC, and SAR values that added solution alkalinity had a soil-specific response and that hydraulic reduction was a function of pH, EC, SAR, clay content and solution alkalinity. A Levenberg–Marquardt optimisation approach was employed by Ali et al. (2019b) that included pH, EC and clay content, although they discussed that while HYDRUS is a physically based model, for the dynamic decline of soil hydraulic conductivity, there is no physical parameter that can be used. This means soil-specific nuances cannot be captured in the model from a physical basis, which was observed also by Ezlit et al. (2013). As with numerous studies (Bennett & Raine, 2012b; Ezlit et al., 2013; McNeal & Coleman, 1966; Quirk & Schofield, 1955; Shainberg et al., 1981), Ezlit et al. (2013) state that saturated hydraulic conductivity (K_s) reduction due to ESP and EC is correlated to clay swelling and dispersion, with the extent of reduction being soil-specific. They subsequently present a semi-empirical model that fits a hydraulic reduction surface to observed data, although this model does not contain pH as a factor.

Therefore, this research aimed to investigate the effect of increasing alkalinity of irrigation water on the soil chemistry and hydraulic conductivity reduction in comparison with the Ezlit et al. (2013) disaggregation model for semi-empirical evaluation of sodic and saline water impact on soil hydraulic reduction. Specifically, the work seeks to incorporate the effect of alkalinity into the disaggregation model via testing the following hypothesis:

$$C_{TH}(EC, SAR, pH) = C_{TH}(EC, SAR_{adj}) \quad \textbf{Equation 6.19}$$

where C_{TH} is the threshold electrolyte concentration for a given soil as either a function of EC, SAR and pH, or as a function EC and an SAR_{adj}. The SAR_{adj} is based on the practical assumption that $CaCO_3$ will precipitate from waters containing high HCO_3^- and CO_3^{2-}, meaning the available Ca^{2+} is decreased. Should the hypothesis hold, then a use of SAR_{adj} provides a simple correction for alkalinity in the Ezlit et al. (2013) model.

7.2. Methodology

7.2.1. Soil selection and characteristic analysis

Soils (two Luvisols, a Vertisol and an Acrisol) were collected from 0–30 cm depth from Queensland and New South Wales states in Australia (**Error! Reference source not found.**). The s oils were selected based on their difference mainly in initial pH and alkalinity, as well as clay mineralogy. The soils were air-dried and gently ground to pass a 2 mm sieve. Using standard methods from Rayment and Lyons (2011), the electrical conductivity (Method 3A1), pH (Method 4A1) were measured in 1:5 soil: deionised (DI) water mix using Radiometer analytical ION 450m. The alkalinity was determined using a Radiometer Analytical Titrator (TIM845, Titration Manager). The water extractions for soluble cations were centrifuged for 30 minutes and analysed on a Perkin Elmer NexIon-ICP MS (Inductively Coupled Plasma – Mass Spectrometer) to calculate SAR (Rayment & Lyons, 2011). For exchangeable cations analysis, the soluble salts were pre-washed with deionised water and then the samples were extracted with 1M NH_4Cl pH adjusted to match the pH of the soil analysed (Marchuk & Rengasamy, 2012). Based on the published procedures the soil particle size was determined using the method of Gee and Bauder (1986), organic carbon by the Walkley-Black method (Walkley & Black, 1934), clay mineralogy by X-ray diffraction described in Dang et al. (2018b). The initial soil physical and chemical properties are presented in and mineralogical composition presented in Table 6.4.

Table 6.4 Physical and chemical properties of selected soils.

Soil	*units*	*Soil 1*	*Soil 2*	*Soil 3*	*Soil 4*
pH (1:5)		8.9	8.8	7.3	4.5
EC (1:5)	$(dS.m^{-1})$	0.34	0.3	0.19	0.08
Clay	%	29	34	62	15
Silt	%	13	16	16	23
Sand	%	59	50	22	63
Soil texture		Clay loam	Clay loam	Clay	Loam
Total alkalinity	$mg.L^{-1}$	207	157	75	0
Organic carbon	%	1.1	1.6	1.3	1.5
Chloride (Cl^-)	$mg.L^{-1}$	174	60	120	33
Nitrate (NO_3-N)	$mg.L^{-1}$	18	60	17	1
CEC	$(cmol_c\ kg^{-1})$	22.6	25.4	64.7	1.79
EDP	%	4.4	13.4	2.2	5.2
CROSS[‡]	$(mmol_c.L^{-1})^{0.5}$	2.5	4.6	3.5	1.2
ECR	%	11.7	15.3	2.6	6.3
ESP	%	3.0	10.6	0.2	3.2
SAR	$(mmol_c.L^{-1})^{0.5}$	1.9	4.3	3.1	0.9
Taxonomic class					
Australian[†]		Brown Dermosol	Red Dermosol	Black Vertosol	Grey Kurosol
World Reference Base		Brown Luvisol	Red Luvisol	Black Vertisol	Grey Acrisol

[‡] Cation Ratio of Soil Structural Stability (CROSS) (Rengasamy & Marchuk, 2011)
[†] Australian Soil Classification (Isbell & NCST, 2016)

Table 6.5 Mineralogical composition of clays (%) from X-Ray diffraction analysis.

Soil	*Montmorillonite*	*Kaolinite*	*Illite/Mica*	*Albite*	*Quartz*
Soil 1	15	30	13	–	42
Soil 2	13	34	-		53
Soil 3	60	7	-	-	33
Soil 4	3	35	–	13	49

7.2.2. Experimental design

The C_{TH} was measured based on the procedure of Bennett and Raine (2012b) and using the mathematical disaggregation model of Ezlit et al. (2013). The C_{TH} procedure was modified by adjusting solutions with various levels of alkalinity (HCO_3^- at 0, 100, 400, and 1000 mg L^{-1}) using $NaHCO_3$. These values were selected based on the threshold level of alkalinity for irrigation water in Australia (100 mg L^{-1}) (ANZECC, 2000), the alkalinity level of most Australian groundwater (~400 mg L^{-1}) (Biggs et al., 2012) and untreated CSG water (~1000 mg L^{-1}) (Kinnon et al., 2010).

The solutions applied to the soils consisted of five values of cation concentration (5, 10, 20, 40 and 80 mmol$_c$ L^{-1}) and up to ten sequentially increasing values of SAR treatments from 0 to ∞ Table 6.6. An ion mixed concentration approach was used to obtain the desired level of EC and SAR solution water by mixing $CaCl_2.2H_2O$, and NaCl compounds with deionised water, and mixing $CaCl_2.2H_2O$, NaCl and $NaHCO_3$ to obtain the desired levels of EC, SAR and alkalinity. The EC, SAR and alkalinity of solutions were determined after solution preparation. SAR values were calculated using Equation 6.20, and adjusted SAR (SAR_{adj}) as per Equation 6.21, based on the method of Lesch and Suarez (2009).

$$SAR = \frac{[Na]}{\sqrt{0.5([Ca]+[Mg])}}$$ **Equation 6.20**

$$SAR_{adj} = \frac{[Na]}{\sqrt{0.5([Ca_{eq}]+[Mg])}}$$ **Equation 6.21**

$$Ca_{eq} = 10^{log\,(X)} \times \left(P_{CO_2}\right)^{1/3}$$ **Equation 6.22**

$$\log(X) = \frac{1}{3}\left[4.6629 + 0.6103 log(I_s) + 0.0844\{log(I_s)\}^2 + 2 log\left(\frac{Ca}{(2HCO_3)}\right)\right]$$ **Equation 6.23**

$$I_s = \frac{(1.3477 \times CC + 0.5355)}{1000}$$ **Equation 6.24**

where square brackets indicate cation concentration (mmol$_c$ L^{-1}). The unit of measure is (mmol$_c$ L^{-1})$^{0.5}$ for SAR and SAR$_{adj}$. Ca_{eq} represents the expected Ca concentration after equilibrating with the bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) during solution application; I_s is ionic strength (μ) and CC indicates the total cation concentration cations in mmol$_c$ L^{-1} and P_{CO_2} represents the partial CO_2 pressure in the near surface soil.

Five soil columns were packed for each soil and each soil column was dedicated to only one of five EC values. An exception here was where the C_{TH} for alkalinity 400 and 1000 mg L^{-1} was investigated because CC of 5 mmol_c L^{-1} (400 mg L^{-1} alkalinity), and 5 and 10 mmol_c L^{-1} (1000 mg L^{-1} alkalinity) was not physically possible using $NaHCO_3$ as the alkalinity source for these concentrations.

The ground soils were carefully packed into polyvinyl chloride (PVC) pipes (inner-diameter 87.5 mm, length 100 mm) to form 50 mm height soil columns for each soil. The long pipe length was used due to the tendency for smectitic clays to swell upon wetting. The pipes were supported with a fine and flexible plastic mesh at the lower end of each core. A fast filter paper (Whatman No.1) was placed at the bottom of the soil columns and the columns were carefully filled with soils and then compacted in layers to ensure homogenous packing for all soils to achieve bulk density around 1.4 gm.cm^{-3}. The columns were covered with a further filter paper to avoid soil surface disturbance during experimentation. Three replicates for each soil were used to determine C_{TH}, creating a total of 204 soil cores for all soils used in this study.

Each soil column was initially wetted overnight from the bottom by capillary tension using pre-treatment calcium chloride (CC = 20 mmol_c L^{-1}) following the method of Ezlit et al. (2013), Menezes et al. (2014), (Dang et al., 2018a) and Bennett et al. (2019a). The soil columns were then removed from the pre-treatment bath and placed in Buchner funnels to collect leachate from the bottom of soil columns. All soil columns were initially equilibrated with the solution $CaCl_2$ solutions to determine the variability between cores, and subsequently reducing erroneous. Then the columns were leached with 1500 mL of the same $CaCl_2$ solution but applied from the top of soil columns. A constant ponded head of 20 mm was achieved and maintained via a Mariotte bottle. The soil columns were then allowed to drain for 2 hours after the first pre-treatment was applied and then a further 1500 mL of the pre-treatment solution was applied until a steady state was achieved for determination of saturated hydraulic conductivity (K_s). Steady state was defined as being reached when less than 3% variation was obtained between 5 consecutive readings. The drainage period allowed for slaking and column settling to occur at the outset, with drainage from saturated condition subsequently avoided for all further solutions. This was followed by the application of a range of solutions of salinity 5 to 80 mmol_c L^{-1} of $CaCl_2$ (SAR = 0, and $HCO_3^- = 0$) to establish the benchmark for K_s, without 2 hours drainage period for solutions. Subsequently, a range of sequence increasing SAR from 0 to ∞, for non-alkaline treated and treated with 100, 400 and 1000 mg L^{-1} solutions. The K_s was measured with a constant head (20 mm) for each solution applied as for the pre-treatment solution has percolated.

The constant head method (Klute, 1965) was used to measure K_s. The outflow leachate was collected in beakers at the bottom of the column at contiguous time intervals until a constant flux was recorded for each solution. The K_s for a vertical soil core under the constant head was determined using Darcy's equation (Equation 6.25).

$$K_s = \frac{VL}{AHt}$$ **Equation 6.25**

Where K_s is saturated hydraulic conductivity (cm.hr^{-1}), V is the volume of solution at steady state (cm^3), L is the length of the soil column (cm), A is the area of the soil column (cm^2), H is the water head from base of core to top of solution (cm), and t is the time for V to flow through soil. The relative saturated hydraulic conductivity (r_{Ks}) was then calculated by dividing the K_s of the SAR $\geq$ 0 solution by the K_s determined for the SAR0 solution applied to each soil column.

The r_{Ks} data were fitted with the disaggregation model from Ezlit et al. (2013) (Equation 6.26) as a function of EC and ESP. The SAR value of each solution was converted to ESP based on the formula suggested by US Salinity Laboratory Staff (1954). The disaggregation model relates steady-state hydraulic conductivity occurring for a given SAR and EC to the most stable condition of the soil to formulate a 3-dimensional hydraulic reduction surface using TableCurve 3D V4.0 graphing program to visualise the response. The MATLAB R2015 mathematical program was then used to extract the reduction contours, which represents the soil specific C_{TH} association.

$$r_{K_s} = 1 - \left(\frac{g e^{m\left(\frac{ESP}{100}\right)} x_o^{\left(\left(\frac{ESP}{100}\right)^a + b\right)}}{1 + g e^{m\left(\frac{ESP}{100}\right)} x_o^{\left(\left(\frac{ESP}{100}\right)^a + b\right)}} \right) at\ x_o > 0$$ **Equation 6.26**

$$r_{K_s} = 1, \qquad at\ x_o \leq 0$$ **Equation 6.27**

where r_{Ks} is the relative 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 r_{Ks} dynamics; and, g, m, a, and b, are all optimisable empirical fitted parameters dependent on soil type.

Table 6.6 Solution composition used to determine threshold electrolyte concentration (Ezlit et al., 2013) model. For each EC and SAR solutions in groups 1 to 9, the alkalinity HCO_3^- was adjustment to 100, 400, and 1000 mg L^{-1}) respectively.

Experimental solutions No.	*Total cation concentration ($mmol_c L^{-1}$)*	*SAR ($mmol_c L^{-1}$)$^{0.5}$*	*Experimental solutions No.*	*Total cation concentration ($mmol_c L^{-1}$)*	*SAR ($mmol_c L^{-1}$)$^{0.5}$*
0	5	0	**5**	5	11.85
	10	0		10	16.76
	20	0		20	23.70
	40	0		40	33.52
	80	0		80	47.40
1	5	1.5	**6**	5	15.70
	10	2.12		10	22.21
	20	3		20	31.42
	40	4.24		40	44.43
	80	6		80	62.83
2	5	3.226	**7**	5	20.01
	10	4.56		10	28.31
	20	6.45		20	40.04
	40	9.13		40	56.62
	80	12.9		80	80.08
3	5	5.4	**8**	5	25.42
	10	7.64		10	35.94
	20	10.80		20	50.83
	40	15.27		40	71.89
	80	21.6		80	101.67
4	5	8.36	**9**	5	Infinity
	10	11.83		10	Infinity
	20	16.72		20	Infinity
	40	23.65		40	Infinity
	80	33.45		80	Infinity

7.2.3. Statistical analysis

The C_{TH} datasets for both SAR and $\mathrm{SAR_{adj}}$ were plotted and a linear regression line was fitted using a calculated Pearson's product-moment correlation coefficient. Direct comparison of this linear regression was subsequently undertaken. Three-dimensional surfaces were created in TableCurve 3D (SYSTAT Software Inc, 2002) with the fit and fitted standard deviation analysed. The full set of hydraulic data for both SAR and $\mathrm{SAR_{adj}}$ systems were plotted with the root mean square error (RMSE) provided as a measure of the data variability, while the Euclidean distance to the line y=x was used to determine data deviation from the line, with two standard deviations (2σ) utilized as the measure for data spread from this line.

7.3. Results

Three-dimensional graphs were produced for K_s reduction without correction (Figure 6.4, Figure 6.5, Figure 6.6 and Figure 6.7), with the contours for 20% K_s reduction (i.e. r_{Ks}=0.8) subsequently extracted for each soil and alkalinity concentration (Figure 6.8). In Figure 6.8, the SAR is calculated as per Equation 6.20 without any adjustment for solution alkalinity in order to display the effect of solution alkalinity on the SAR without correction. Figure 6.9 displays the same data with $\mathrm{SAR_{adj}}$ to test the hypothesis that the C_{TH} for a given soil without solution alkalinity is equivalent to the C_{TH} for solutions containing alkalinity provided the $\mathrm{SAR_{adj}}$ (Equation 6.21) is applied as a correction.

Soil-specific response to solution salinity, sodicity, and alkalinity was observed for the four soils. For all soil types the K_s of the soil was maintained at higher levels when leaching occurred with solutions containing greater EC and no alkalinity, as compared to either decreasing the EC or increasing the alkalinity. There was an affinity for K_s reduction at low electrolyte concentration and increasing SAR level. Based on the results of this work, the hypothesis is able to be accepted for (Figure 6.10).

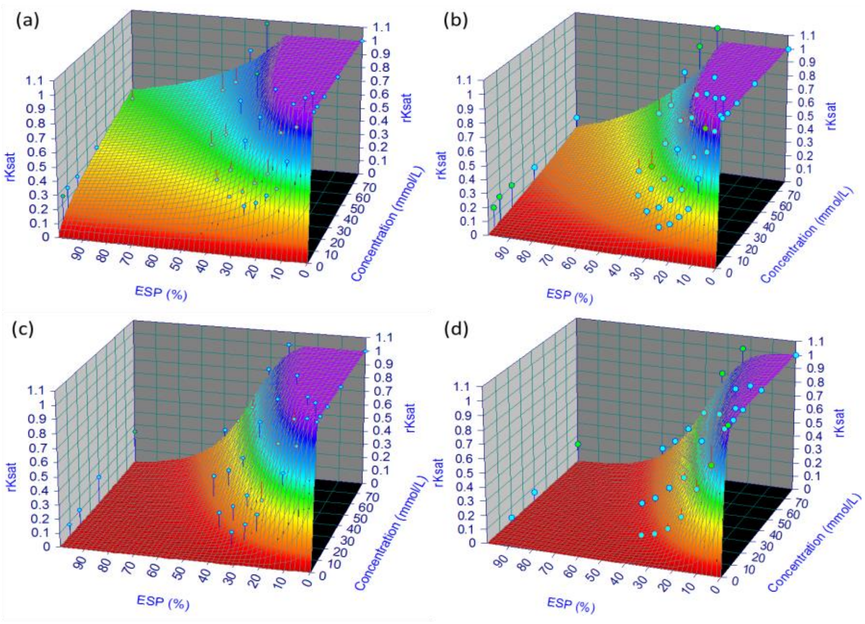

Figure 6.4 Relative saturated hydraulic conductivity (r_{Ks}) for Soil 1 treated with alkalinity at a) 0 mg L^{-1}, b) 100 mg L^{-1}, c) 400 mg L^{-1}, and d) 1000 mg L^{-1}. The 3-Dimensional surfaces are function of the exchangeable sodium percentage (ESP) and solution cation concentration ($mmol_c$ L^{-1}) as calculated using the approach of Ezlit et al. (2013) model. The surface mesh and blue points represent the fitted model and observed r_{Ks} values, respectively. Model parameters and associated statistics are presented in Table 6.7.

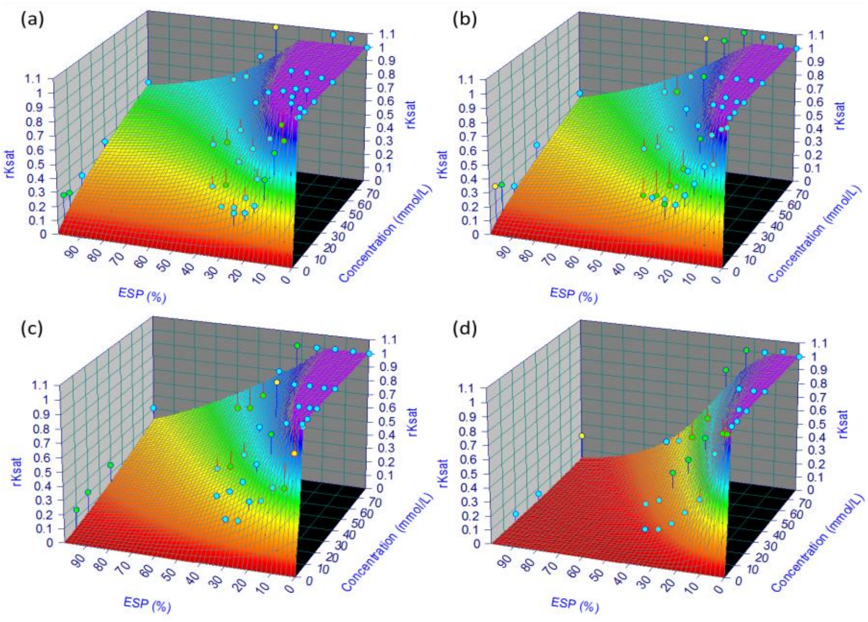

Figure 6.5 Relative saturated hydraulic conductivity (r_{Ks}) for Soil 2 treated with alkalinity at a) 0 mg L^{-1}, b) 100 mg L^{-1}, c) 400 mg L^{-1}, and d) 1000 mg L^{-1}. The 3-Dimensional surfaces are function of the exchangeable sodium percentage (ESP) and solution cation concentration ($mmol_c$ L^{-1}) as calculated using the approach of Ezlit et al. (2013). The surface mesh and blue points represent the fitted model and observed r_{Ks} values, respectively. Model parameters and associated statistics are presented in Table 6.7.

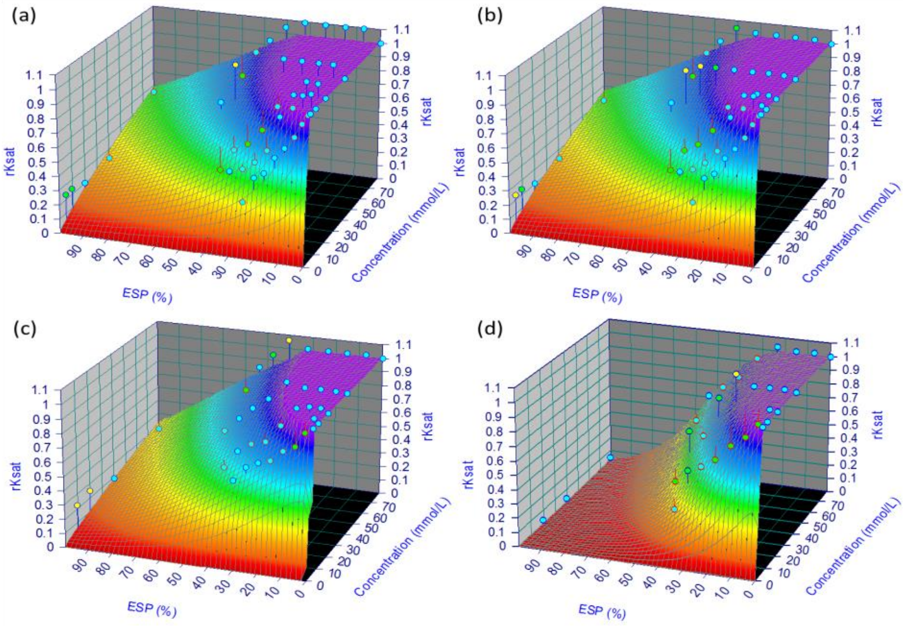

Figure 6.6 Relative saturated hydraulic conductivity (r_{Ks}) for Soil 3 treated with alkalinity at a) 0 mg L^{-1}, b) 100 mg L^{-1}, c) 400 mg L^{-1}, and d) 1000 mg L^{-1}. The 3-Dimensional surfaces are function of the exchangeable sodium percentage (ESP) and solution cation concentration (mmol$_c$ L^{-1}) as calculated using the approach of Ezlit et al. (2013). The surface mesh and blue points represent the fitted model and observed r_{Ks} values, respectively. Model parameters and associated statistics are presented in Table 6.7.

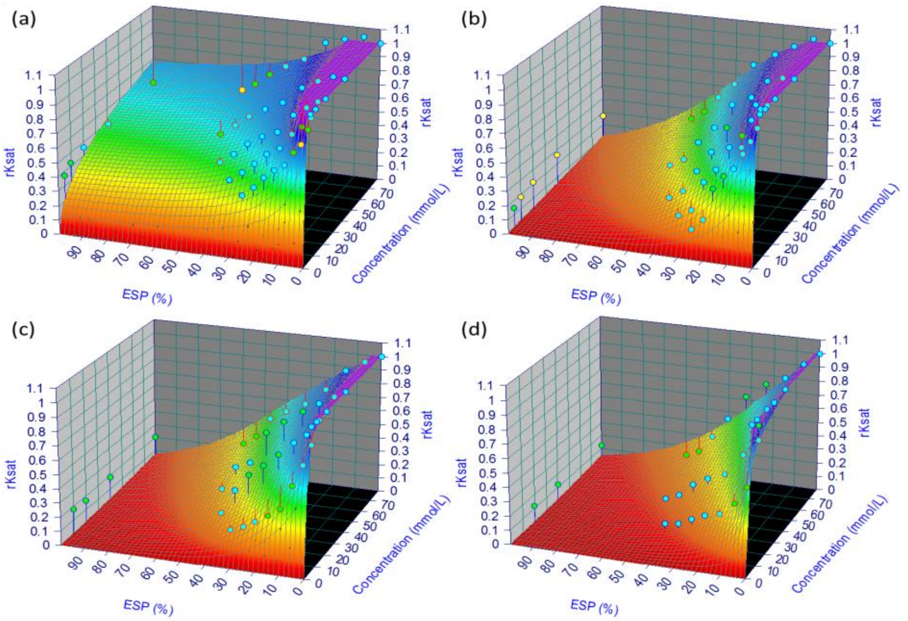

Figure 6.7 Relative saturated hydraulic conductivity (r_{Ks}) for Soil 4 treated with alkalinity at a) 0 mg L^{-1}, b) 100 mg L^{-1}, c) 400 mg L^{-1}, and d) 1000 mg L^{-1}. The 3-Dimensional surfaces are function of the exchangeable sodium percentage (ESP) and solution cation concentration (mmol$_c$ L^{-1}) as calculated using the approach of Ezlit et al. (2013). The surface mesh and blue points represent the fitted model and observed r_{Ks} values, respectively. Model parameters and associated statistics are presented in Table 6.7.

7.3.1. Threshold electrolyte concentration without correction

The C_{TH} data for the four soils (Figure 6.8) supports a soil specific response. The higher clay content Vertisol (Soil 3) had the most resilience to increasing solution quality marginality, while the higher sand content Acrisol (Soil 4) had the lowest, and the Dermosols behaved similarly. This might suggest an explanation where the soil initial pH, pH buffering capacity, clay content and/or mineralogy define the resultant hydraulic reduction. While it is likely these factors have some influence, there is insufficient data in this work to draw definitive conclusions. Furthermore, the work of demonstrated that the soil order was not a useful predictor of the resultant C_{TH}. Although this is not unexpected as the attributes used to determine taxonomic divisions in classification schemes do not necessarily have a determinative relationship to K_s.

Table 6.7 Model parameters for the fitted surface predicted through TableCurve for soils in Figure 6.4, Figure 6.5, Figure 6.6 and Figure 6.7.

Soils	*Alkalinity (mg L^{-1})*	*Model parameters*							R^2	*Predicted* R^2	*Fitted standard error*	F_{stat}
		a	*b*	*g*	*m*	*f*	*s*	*l*				
Soil 1	**0**	$1.9X10^{-5}$	$2.3X10^{-3}$	7.76	-0.35	0.403	9.58	-9.56	0.85	0.82	0.149	38.95
	100	0.267	0.322	4.454	1.077	0.799	8.89	-8.86	0.93	0.91	0.105	90.2
	400	0.999	1.66	4.436	4.95	0.853	9.49	-18.21	0.8	0.76	0.219	22.37
	1000	0.611	1.99	5.47	5.65	0.74	1.70	-6.51	0.98	0.97	0.071	162.67
Soil 2	**0**	$2.3X10^{-7}$	0.19	9.26	-0.86	0.58	8.69	-8.25	0.93	0.91	0.093	88.72
	100	$2.1X10^{-5}$	0.22	6.65	0.021	0.452	5.84	-6.71	0.90	0.88	0.099	62.79
	400	0.354	0.599	6.01	0.869	0.544	6.997	-11.26	0.91	0.89	0.097	59.67
	1000	0.237	1.44	22.42	2.199	0.665	2.665	-4.52	0.97	0.96	0.077	119.15
Soil 3	**0**	$8.2X10^{-6}$	0.152	4.12	0.937	0.295	11.59	-16.78	0.88	0.86	0.105	52.6
	100	$2.1X10^{-7}$	0.185	4.387	1.06	0.273	10.38	-15.11	0.92	0.90	0.083	76.88
	400	0.306	0.058	1.421	3.147	0.154	12.38	-19.93	0.95	0.94	0.058	112.84
	1000	0.406	0.749	29.69	6.96	0.0317	7.31	-11.78	0.95	0.93	0.081	77.96
Soil 4	**0**	0.031	$6.1X10^{-7}$	6.03	-0.88	0.311	3.55	-1.326	0.86	0.84	0.080	43.61
	100	$1.3X10^{-6}$	0.213	4.64	2.39	0.32	2.47	-4.33	0.94	0.93	0.075	116.32
	400	0.46	0.537	3.11	3.60	0.36	1.92	-3.08	0.91	0.89	0.090	54.8
	1000	0.306	1.037	2123.9	3.2	0.030	0.778	-1.254	0.97	0.96	0.060	143.1

For Soil 1 and 2, the SAR value at the C_{TH} (0 through 1000 mg L^{-1}) of 2.0 dS m^{-1} — an arbitrary concentration consistent with groundwater irrigation concentration regularly sought to be used — was ~21 for zero alkalinity (Alk_{0}), ~18 for alkalinity at 100 mg L^{-1} (Alk_{100}), ~13 for alkalinity at 400 mg L^{-1} (Alk_{400}), and ~8 for alkalinity at 1000 mg L^{-1} (Alk_{1000}) curves (Figure 6.8). In contrast, for Soil 3 at the same C_{TH} the SAR values were 29, 28, 25, and 20 for Alk_{0}, Alk_{100}, Alk_{400}, and Alk_{1000}, while for Soil 4 these SAR values were 16, 12, 5, and 2, for the respective sequence of solution alkalinity. For any SAR value greater than these values, it is required to either reduce the solution alkalinity level or increase the salinity of the irrigation water to avoid further K_s reduction. Importantly, these results clearly demonstrate that the solution alkalinity must be taken into account when reporting the C_{TH}.

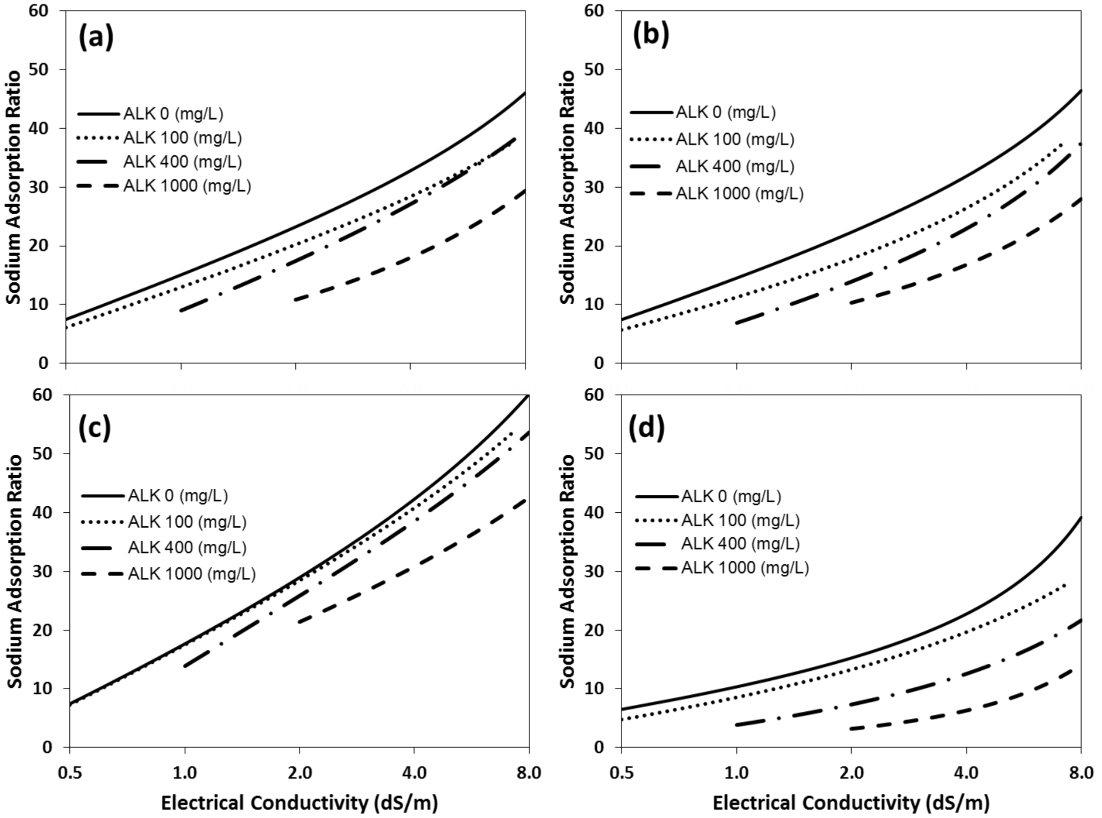

Figure 6.8 The threshold electrolyte concentration curves ($0.8r_{Ks}$) produced at different levels of alkalinity for a) Soil 1, b) Soil 2, c) Soil 3 and d) Soil 4. N.B. the x-axis is logarithmic with base 2. The curves shown were derived from surface fitting modelling of Ezlit et al. (2013).

7.3.2. Correcting for alkalinity concentration

With the correction applied to the data in Figure 6.8 it was observed that the C_{TH} data for the alkaline solutions became approximately equivalent to the C_{TH} with zero solution alkalinity (Figure 6.9), compared on the basis of C_{TH} being a 20% r_{Ks}. Correcting the SAR to SAR$_{\text{adj}}$ (Equation 6.21) results in an increased SAR value, which is to be expected. This subsequently allowed the observed K_s reduction data (r_{Ks}) from soil treated with solutions containing zero alkalinity to be extracted and plotted against the observed hydraulic reduction data at the equivalent SAR$_{\text{adj}}$ from the corresponding fitted models (Figure 6.10). The resultant fit suggests a near 1:1 relationship between these data, which allows the hypothesis to be accepted. There is increased deviation from the 1:1 line as the SAR and alkalinity is increased (i.e. SAR$_{\text{adj}}$ increases). This is due to the residual error associated with the disaggregation model surface fitting procedure.

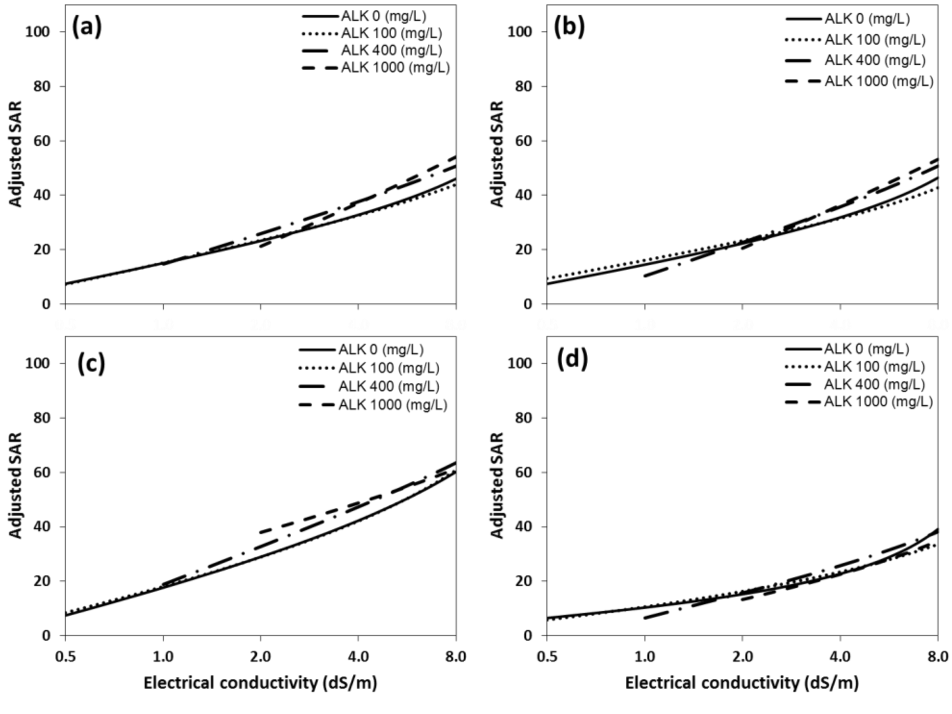

Figure 6.9 Threshold electrolyte concentration (C_{TH}) or 0.8r$_{\text{Ks}}$ produced by solutions treated with 0, 100, 400, and 1000 mg L^{-1} of alkalinity (HCO_3^-) at electrical conductivity of 0.5, 1, 2, 4, and 8 dS m^{-1} and adjusted sodium adsorption ratio 0 to ∞. Where (a) is Soil 1, (b) Soil 2, (c) Soil 3, and (d) Soil 4. The curves shown were derived from surface fitting modelling of Ezlit et al. (2013).

7.3.3. Effect of solution alkalinity on soil stability in a pure sodium solution

For the C_{TH} measured without solution alkalinity, it was observed that the four soils maintained a K_s between 30 and 50% reduction (0.7 to 0.5 r_{Ks}) from the initial K_s in a pure Na solution, where the EC was 8.0 dS m^{-1} (Figure 6.4, Figure 6.5, Figure 6.6 and Figure 6.7). Increasing the alkalinity within solution for these same soils at the equivalent SAR and EC resulted in progressive decrease in K_s with all soils exhibiting >90% reduction (<0.1 r_{Ks}) as solution alkalinity of to 1000 mg L^{-1}. This demonstrates that the addition of alkalinity to the percolating solution decreases the general resilience of the soils to withstand the effects of marginal quality irrigation water.

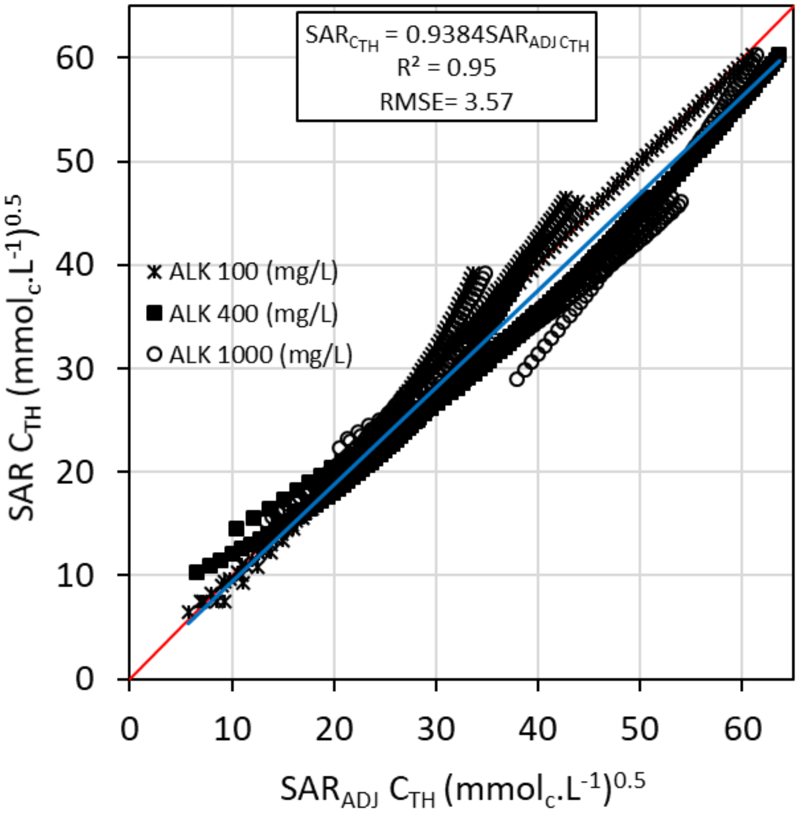

Figure 6.10 The relationship between threshold electrolyte concentration (C_{TH}) or 0.8r_{Ks} calculated using sodium adsorption ratio (SAR) and adjusted sodium adsorption ratio (SAR_{adj}). The diagonal red line represents the 1:1 line and the blue line is the regression fit for the observed data. RMSE is root mean square error for the data set against the 1:1 line.

To investigate the extent that the *SAR_{adj}* deviated from the *SAR* system data, the semi-empirical equations of the four soils were compared and plotted in Figure 6.11. From this data it was possible to determine the threshold where the data commenced a rapid increase in deviation from the *y=x* line.

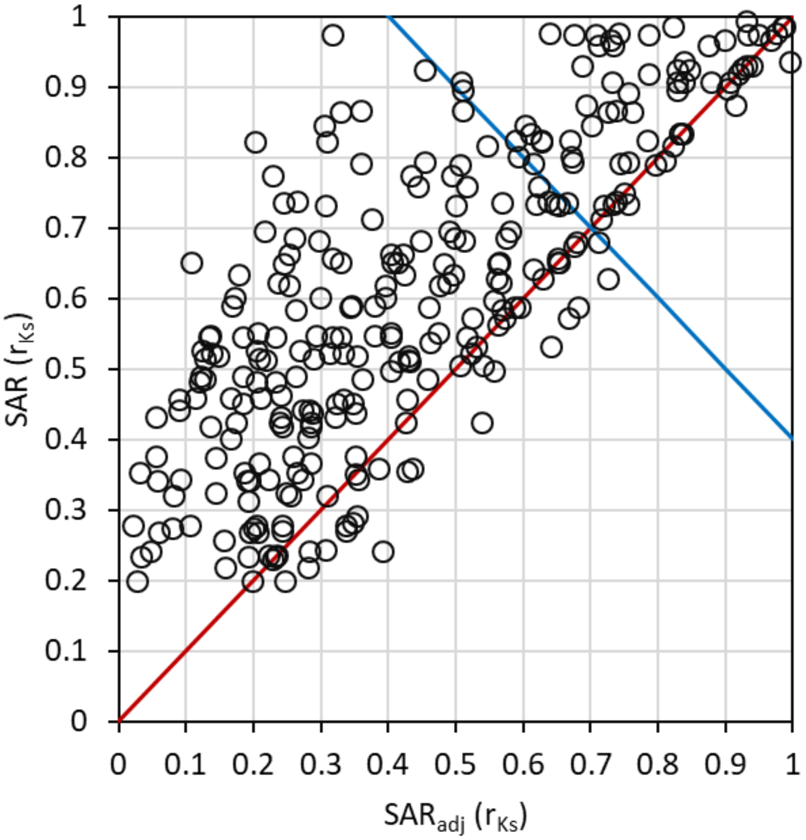

Figure 6.11 Relative saturated hydraulic conductivity (*r_{Ks}*) observed for the sodium adsorption ratio (SAR) and adjusted sodium adsorption ratio (SAR_{adj}) systems for all soils, plotted against the line y=x (red line), with the line y=-x (blue line) intercepting the data at the threshold of increasing variability (y=0.7, x=0.7).

This was proximal to the point where y and x=0.7. Table 6.8 contains the descriptive statistic for the full dataset and the data split around this point. Where y and x<0.7 ($r_{Ks}<0.7$) the RMSE of the data increased by $r_{Ks}=0.104$ and $2\sigma_{ED}$ increased by $r_{Ks}=0.108$, in comparison to the data set where y and x≥0.7 ($r_{Ks}\geq0.7$). These data (Table 6.8, Figure 6.4, Figure 6.5, Figure 6.6, Figure 6.7, Figure 6.10 and Figure 6.11) suggest that solution alkalinity is having a greater effect on the soil stability of the system than is accounted for in adjusting the system for precipitation of calcium and magnesium.

7.4. Discussion

7.4.1. Threshold electrolyte concentration and incorporation of alkalinity into the disaggregation model

This study sought to test the hypothesis that the threshold concentration of a Na:Ca system containing alkalinity (i.e. C_{THadj}) was equivalent to the C_{TH} of a Na:Ca system devoid of solution alkalinity (Equation 6.19), via use of the adjusted SAR (SAR_{adj}), as defined by Lesch and Suarez (2009) for the contribution of HCO_3^- (Equation 6.21). In doing so, incorporation of HCO_3^- directly into the disaggregation model of Ezlit et al. (2013) was further considered. Evidence allowing the acceptance of our hypothesis was obtained in this work (Figure 6.9 and Figure 6.10), provided the hydraulic reduction defining the C_{TH} was in the range of 10–30% ($0.7 \leq r_{Ks} \leq 0.9$; Table 6.8 and Figure 6.11); 10% is used as the upper bound here on the basis that hydraulic decrease must be measurable for the C_{TH} to be defined (Quirk and Schofield 1955). Where hydraulic reduction was greater than 30% ($r_{Ks}<0.7$) the SAR and SAR_{adj} for the equivalent r_{Ks} diverged significantly, suggesting that judicious consideration is required for the incorporation of the Lesch and Suarez (2009) equation directly into the Ezlit et al. (2013) disaggregation model.

Table 6.8 Descriptive statistics for the full data set from Figure 6.11 of the four soils (Total) and where the reduction in hydraulic conductivity (r_{Ks}) is used to split the data set; *n*, number of observations; *n%*, number of observations as a percentage; *Min* and *Max*, the minimum and maximum value for the data sets, respectively; *AED*, average Euclidean distance from the line y=x; $2\sigma_{ED}$, two standard deviations of the Euclidean distance; *RMSE*, root mean square error of the data set.

Data set	*n*	*n%*	*Min*	*Max*	*AED*	$2\sigma_{ED}$	*RMSE*
Total	480	100	$1.08x10^{-19}$	0.46	0.086	0.205	0.19
$r_{Ks} \geqslant 0.7$	293	61	$3.01x10^{-10}$	0.46	0.065	0.154	0.17
$r_{Ks}<0.7$	182	39	$1.08x10^{-19}$	0.29	0.11	0.182	0.21

Given the boundary condition in accepting the hypothesis, we consider the case of the use of the Lesch and Suarez (2009) equation for SAR_{adj} from the perspective of predictive capability and semi-empirical modelling. Our data suggests the correction for SAR_{adj} is only valid — in terms of direct equivalence to the Na:Ca system devoid of alkalinity — for $0.7 \leq r_{Ks} \leq 0.9$. This implies that one could undertake C_{TH} as described by Ezlit et al. (2013), obtain the hydraulic reduction for a system not containing solution alkalinity, and directly correct SAR to $\mathrm{SAR_{adj}}$ for the data range where $r_{Ks} \geq 0.7$. This would provide a predictive capability for the inclusion of alkalinity. That is, for:

Equation 6.28

$$SAR_{Ezlit} = f\left(Na, Ca, EC, r_{K_s}\right)$$

where SAR_{Ezlit} indicates the SAR output of the Ezlit et al. (2013) model for a Na:Ca system without alkalinity. Substitute Equation 6.22 for the *Ca* term in Equation 6.28 to adjust the SAR_{Ezlit}:

Equation 6.29

$$SAR_{Ezlit_{adj}} = f\left(Na, Ca_{eq}, EC, r_{K_s}\right)$$

where Ca_{eq} is the Lesch and Suarez (2009) term, and all other terms in the function remain unchanged from the Ezlit et al. (2013) model (i.e. equivalent between Equation 6.28 and Equation 6.29). This subsequently allows the simplified C_{TH} to be determined semi-empircally, and the effect of varying alkalinity concentrations on the C_{TH} system to be predicted, using Equation 6.21 to correct SAR_{Ezlit} to SAR_{adj}, provided the $r_{Ks} \geq 0.7$.

The C_{TH} is somewhat of an arbitrary value as it represents a measurable departure from a potential minima defined as the condition of absolute stability (Bennett et al., 2019a). This has led to different levels of K_s reduction to select a practical C_{TH} value, whereby Quirk and Schofield (1955) suggested 10%, 15% later suggested by Quirk (2001), 20% used by multiple authors (Bennett & Raine, 2012b; Dang et al., 2018a; Ezlit et al., 2013), and 25% as suggested by McNeal and Coleman (1966) as an indicator for C_{TH} position. On the other hand, Menezes et al. (2014) reported that up to 80% reduction in K_s for soils with considerably high initial K_s (e.g. coarse-textured soils) may well be acceptable, but did not suggest this to be the C_{TH}, rather a practical limit based on the system function. As the results indicate that the SAR correction should only be advised as valid to determine C_{TH} based on the above assumptions where C_{TH}<30% K_s reduction, and an effect beyond that considered in the Lesch and Suarez (2009) term for hydraulic reduction is observed past this point, a predictive capability is not possible. However, it is prudent to consider the validity of the results in terms of a real-world functioning system. The results in Figure 6.4, Figure 6.5, Figure 6.6 and Figure 6.7 are all observed results based upon a Na:Ca system with increasing levels of alkalinity. In this sense, the reduction is real, and, for example, an 80% reduction in K_s would occur sooner in the soil system given solution alkalinity than for the equivalent soil system devoid of alkalinity. This would have substantially changed the solution recommendations from the Menezes et al. (2014) work in terms of practical irrigation. Therefore, if alkalinity solutions are to be applied to land without treatment for alkalinity, then the effect of this alkalinity can be demonstrated using a semi-empirical approach to provide the 3-dimensional hydraulic reduction surface at a given alkalinity, as was demonstrated in this work.

7.4.2. Alkaline irrigation water effect on soil structural decline

There is clear evidence that the presence of HCO_3^- in the soil system results in K_s reduction as the concentration of HCO_3^- increases, for a given level of solution sodicity and salinity, in comparison to the non-alkaline solutions (Figure 6.8). The difference in r_{Ks} for this increasing alkalinity is purported to be due to a concomitant increase in sodicity, depending on variations in clay content (Ali et al., 2019a; Goldberg & Forster, 1990; McNeal & Coleman, 1966), clay mineral types and organic matter content Bennett et al. (2019a), and the interactions of a mixture of clay minerals (Oster et al., 1980; Sharma & De Datta, 1985). While these factors provide reasoning for the variation in susceptibility to the applied solutions, further confirming the soil-specific effect of hydraulic decline (Bennett et al., 2019a; Dang et al., 2018a), they do not explain the differences in endstates for the alkaline and non-alkaline solutions observed for a pure sodium system (Figure 6.4, Figure 6.5, Figure 6.6 and Figure 6.7). This difference in end state suggests that the solution alkalinity is having an effect beyond the apparent increase in SAR from $CaCO_3$ precipitation.

The differences for the susceptibility of soil structural stability to a given solution are usually acknowledged to be due to variations in clay content (Ali et al., 2019a; Goldberg & Forster, 1990; McNeal & Coleman, 1966; Zhu et al., 2016), clay mineral types and organic matter content (Churchman et al., 1993; Oster et al., 1980; Zhu et al., 2019a). In keeping with this, an increase in the soil system HCO_3^- has been documented to affect the organic matter content and clay mineral suite in the soil system (Goldberg & Glaubig, 1987; Sposito, 2008). When investigating the effects of hydroxide and pH on organic matter dissolution, aggregate breakdown and the subsequent reduction in K_s numerous authors found that the soil K_s reduction due to pH changes will depend on the organic matter dissolution and the quantity of variable charge clay minerals in the soil (Lieffering & McLay, 1996; Nyamangara et al., 2007; Suarez et al., 1984). As organic matter is well understood to act as a binding agent throughout a wide range of aggregate size classes in soils, from clay coatings to greater than 250 µm macro-aggregates (Lieffering & McLay, 1996; Oades, 1984; Tisdall & Oades, 1982), dissolution of organic matter should be expected to result in disaggregation processes, which we suggest has occurred for the soils in this study.

In addition, the increase of alkalinity is expected to enhance the dissolution of clay minerals in the soils (Amram & Ganor, 2005; Berger et al., 1994; Goldberg, 2002), change the charge balance of clay colloids and pH buffering capacity (Nelson & Oades, 1998). For the lower clay content soil, the decrease in relative K_s was faster compared to the higher clay content soils, which may further result from dissolution of quartz that increases with increasing alkalinity/pH of the solution (Bennett, 1991). High solution alkalinity increases the net negative charge resulting in increased inter-particle forces, and reduces the binding action of sesquioxides, which should be expected to cause further K_s reduction (Helling et al., 1964; Rengasamy & Olsson, 1991; Suarez et al., 1984). The current research only used four soils with distinctly different physical, chemical and mineralogical properties, but did not investigate large number of soils with similar properties. Therefore, these effects require further investigation in terms of how they might be included into a model for prediction of hydraulic decline, although highlight that the inclusion of a specified solution alkalinity in semi-empirical approaches such as Ezlit et al. (2013) are prudent to provide indication of alkalinity effects on soils, even at rather low concentrations such as 100 mg L^{-1} of alkalinity.

7.4.3. Considerations for alkaline irrigation water application

This study work suggests that precaution is required in the consideration of alkaline water application to productive lands, which is by no means novel finding (Minhas et al., 2019; Sharma & Minhas, 2005). However, despite scientific understanding of various reduction process that solution alkalinity may have on the soil hydraulic network, there remains a requirement to build this into the tools and management guidelines for irrigation water containing alkalinity. Additionally, not only the interactions of alkalinity with salinity and sodicity need to be considered, but also the effect on mineral and organic matter dissolution. For example, in the Australian irrigation water guidelines (ANZECC, 2000), alkalinity up to and including 100 mg L^{-1} is reported to have no effect on soil structure stability, permeability and plant growth (ANZECC, 2000; DAF, 2014). The results of our work demonstrated that 100 mg L^{-1} of bicarbonate concentration reduced K_s of soils at greater extent than for a soil-irrigation system without alkalinity applied. Additionally, the direct use of high alkalinity waters, such as those derived from the Great Artesian Basin aquifers (Biggs et al., 2012), occurs in many agricultural systems globally. Therefore, it is prudent to determine suitable guidelines, as well as seek the use of semi-empirical models, to correctly prescribe the strategic use of marginal quality saline-sodic and alkaline water.

7.5. Conclusion

This study demonstrates that adjustment of the SAR for alkalinity concentration is useful in the prediction of alkalinity effects on the C_{TH} conditions (SAR, EC) required to maintain the hydraulic conductivity of a soil. However, it also demonstrates that the r_{Ks} was only able to be reliably predicted for $r_{Ks} \geq 0.7$, due to soil structural decline beyond the effect of alkalinity enhancing the apparent SAR. This was likely attributed to increased dissolution of clay minerals and organic matter, but requires further investigation to confirm the additional mechanism/s. The findings further emphasise that management guidelines should consider SAR, EC and alkalinity in the suitability of marginal quality saline-sodic and alkaline irrigation water as a strategic resource.

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8. Planning land management strategies for application of alkaline and sodic groundwater on two soils in New South Wales

8.1. Introduction

The shortage of freshwater resource has increased the use of alkaline and sodic groundwater, as well as industrial waste-waters, in agricultural regions, globally, for irrigation purposes (Ezlit et al., 2013; Sharma & Minhas, 2005). The use of marginal quality irrigation water results in increased risk in the potential for soil structural degradation (Cook et al., 1994; Dang et al., 2018c; Shainberg & Letey, 1984; Zhu et al., 2019a), and consequent reduction in crop production (Burrow et al., 2002; Choudhary et al., 2011; Rengasamy, 2010). The quality of groundwater is often variable within regions and is associated with geological formations that produce water containing high levels of bicarbonate (HCO_3^-) and sodium (Na^+) ions, in comparison to calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions (Biggs et al., 2012; Cartwright et al., 2012; Kinnon et al., 2010). Within Australia, the use of marginal quality saline-sodic and alkaline irrigation water for agricultural production occurs with principal regard to the sodium adsorption ratio (SAR; risk of sodicity) and EC, and very little consideration toward the alkalinity of the water. On the other hand, where these waters are reused from industry, management plans for the solution alkalinity are scrutinised prior to government approval for water reuse (Bennett et al., 2016b; Bennett & Warren, 2015; McKenna et al., 2019). Appropriate management of irrigation water containing alkalinity is required to prevent deterioration of soil physicochemical properties and reduce the negative effects of Na^+ on soil structure. Furthermore, where soil sodicity, salinity and alkalinity already exist as soil constraints, management plans for marginal water become significantly more important, as the immediacy of effect from the application of such water will be enhanced.

Management of irrigation water that is saline-sodic and alkaline is complex and requires the balance of a number of physicochemical aspects, rather than a reductionist approach to management of the individual constraints. The primary concerns for soil structural integrity when irrigating with marginal quality water are sodicity, salinity and alkalinity, which can all lead to deterioration of aggregate stability (swelling, disaggregation and dispersion). These processes can result in a reduction of soil saturated hydraulic conductivity (K_s), susceptibility to surface sealing, and soil aeration reduction (Jackson & Reddy, 2007; Mamedov et al., 2000; Rengasamy & Olsson, 1991). Solution salinity — the concentration of dissolved mineral salts in the irrigation water and soil solution — is often considered to be the most important criteria for assessing irrigation water quality, as it represents a total concentration of ions (Ghassemi et al., 1995), and can have a positive stabilising effect on soil structure via changing the osmotic potential of the soil solution (Quirk & Schofield, 1955); that is, two soils presented with the same percolating solution may respond with one having a negative and the other a positive effect on K_s (Bennett & Warren, 2015). Solution sodium and alkalinity cause deterioration of soil physiochemical properties, depending on the salinity, via swelling, disaggregation and clay particle dispersion as a soil-specific process (Bennett et al., 2019a; Bennett & Raine, 2012b; Marchuk & Rengasamy, 2012). For land previously irrigated with alkaline and sodic water, even where the soil salinity is sufficient to offset the soil structural effects of increased sodicity and alkalinity, rapid dilution of this soil solution occurs with subsequent rainfall, or irrigation with low electrical conductivity (EC), which can result in degradation of the soil structural stability (Dang et al., 2018b; Dang et al., 2018d; Sumner, 1993). This phenomenon can be minimised through buffering the soil system with an electrolyte source, such as gypsum (Ali et al., 2018), or another soluble salt source (Menezes et al., 2014; Suarez et al., 2006). However, irrigation with saline water, or application of soluble salts, can result in reduced crop production when salinity exceeds the threshold level of crop tolerance (Ayers & Westcot, 1985; Hanson et al., 1999; Rengasamy, 2002b). Given that the land application management of such marginal water is complex, and soils respond to these waters on a soil-specific basis, there is a requirement to provide greater field-based examples of marginal groundwater irrigation and the effect of subsequent management practices.

A practical strategy to minimise the effects of Na^+ and HCO_3^- contained in irrigation water and transferred to the soil system, is to apply an acidifying source to neutralise the alkalinity (e.g. sulphur) and a calcium source (e.g. gypsum) to amend the SAR (Bennett et al., 2016b; Ganjegunte et al., 2005; Johnston et al., 2008; McKenna et al., 2019). Many studies have demonstrated that the use of gypsum ($CaSO_4.2H_2O$) as a soil amendment is effective in regulating sodium adsorption ratio (SAR) (Amezketa et al., 2005; Bennett et al., 2014). However, the extent of gypsum effect for soils with comparable sodicity is variable in nature, which is a function of the form of the gypsum applied, (Bennett et al., 2015b; Ghafoor et al., 1989), the amount applied in comparison to the amount required (Page et al., 2018), the soil properties themselves (Bennett et al., 2015a; Dang et al., 2010; Sumner, 1993), and climatic influences. In terms of management of irrigation water containing sodium, the application rate must be sufficient to offset the contained solution sodicity, as well as account for some inefficiency in dissolution and loss via leaching/run-off and/or wind (Bennett et al., 2016b; McKenna et al., 2019). Additionally, treating a solution that is sodic and alkaline with gypsum without first addressing the residual alkalinity results in significant inefficiency as the Ca is consumed in the precipitation of carbonate (Johnston et al., 2013). An acidifying source is first needed to consume the alkalinity and allow any dissolved Ca to remain in solution.

The use of elemental sulphur (S), often applied as a sulphur bentonite prill, to regulate soil alkalinity and pH has received recent attention in the beneficial reuse of highly alkaline groundwater associated with coal seam gas extraction (Bennett et al., 2016b; Johnston et al., 2013; King et al., 2004; McKenna et al., 2019), whereby the sulphur source is converted to sulphuric acid *in situ* via sulphur-oxidising bacteria. The use of sulphuric acid applied in line to the irrigation water source is also effective (Raine & Ezlit, 2010). Ganjegunte et al. (2005) and Vance et al. (2008) amended with gypsum and sulphur to offset the solution sodicity and alkalinity when irrigating with coal seam gas (CSG) water, indicating that the amendments minimised the impact on the soil chemical characteristics controlling soil structure (ESP, EC and SAR), but they did not avoid modification of soil structure. The study of Ganjegunte et al. (2005) also stated that results vary depending on the initial soil physical and chemical properties in particular soil texture. Similarly, a study conducted by Eltaif et al. (2011) shows that reduction in K_s (equivalent to aggregate breakdown) occurred in all soil textures (e.g. clay, clay loam and sandy loam), but in different ratios depending on the initial soil sodicity, irrigation water sources, clay content and clay mineral suite. These studies have indicated that it is possible to maintain soil properties in terms of K_s, infiltration rate and soil aggregate stability for the use of extremely poor quality CSG water. Wei et al. (2006) suggest that elemental sulphur as a soil amendment is recommended when agricultural soil pH exceeds 6.6, although the use of this is limited in the scientific literature for agricultural production. On this basis, a greater body of work focusing on agricultural production is required to assess the environmental and economic efficacy of the approach as well as evaluate the current models to predict the potential changes might occur with utilising these amendments.

Computer modelling to predict the solute movement and reactions of cations and anions in the soil is a potentially valuable approach for agricultural land management (Šimůnek & Suarez, 1997; Šimůnek et al., 2007; Suarez, 2001). Modelling has the potential to assist feasibility assessment of different soil amelioration approaches, in terms of practice efficiency and the efficacy of extending approaches to other similar situations (Qadir et al., 2001b; Šimunek et al., 2012). The HYDRUS software package is perhaps the most commonly used mathematical model for evaluating water flow and associated transport of various chemicals involved within the flowing solution. The HYDRUS-1D program, coupled with the PHREEQC biogeochemical code (HP1) module, considers kinetic chemical reactions, such as the precipitation/dissolution of calcite and the dissolution of dolomite, and is suitable to simulate the ion dynamic change in sodic soils reclaimed by gypsum (Jacques et al., 2013; Ramos et al., 2011; Reading et al., 2012). Šimůnek et al. (2007) argue that these models can be important tools for simulating flow and solute movement in the soil for determining laboratory and field experiments associated with the flow and solute movement. Understanding the mechanisms of land amendment under alkaline irrigation water application, solute movement, and the complex mechanisms associated with alkalinity amelioration in the field condition is crucial in managing soil and water alkalinity. Therefore, this study was carried out to validate the HP1 model for prediction of land amendment mechanisms in the field condition, and to provide a practical assessment of the HYDRUS model on the basis of its potential to plan for alkaline irrigation water land amendment strategies.

The aims of this study were (i) to provide an insight into the efficacy of land amendments using gypsum, sulphur and lime as a management strategy for alkaline and sodic groundwater applied to two Australian agricultural Dermosol soils, as well as any legacy effects that could potentially occur for the long-term and agronomic practices and (ii) to assess the applicability of the HYDRUS-1D model to predict potential changes in the soil solution chemistry in the context of soil amendment strategy.

8.2. Material and Methods

8.2.1. Experimental sites

The experiment studies were conducted at two agricultural farms located in North Star ((Site 1) 28°58'28.7"S, 150°26'49.5"E; and (Site 2) 28°54'59.4"S, 150°16'28.2"E) in New South Wales, Australia (Table 8.1). These sites have a subtropical, and sub-humid climate (Williams et al., 2002) with hot summers and cool winters. Rainfall is concentrated in the summer months with average annual rainfall of 580–610 mm (Bureau of Meteorology, Australia). The soil types at the experimental sites were a brown Dermosol (Site 1) and red Dermosol (Site 2) overlying basalt and minor sediments (Brown, 1995). These lands had been used for growing irrigated wheat and cotton crops. The field texture grade is clay loam throughout the assessed depths (0–40cm). A slight increase in clay content occurred at depth and across the field due to the large scale of the study area, although the texture grade and clay mineral suite are not affected by this. The predominant clay minerals in these soils are kaolinite and montmorillonite, with the existence of some illite in the soil of Site 1 (Table 8.1). The experimental land of Site 1 had ~2% slope from the south towards the north, and ~1.5% from west to east with slight low depressions and rises across the field, while the experimental of Site 2 had a plain landform pattern with <0.5% slope.

8.2.2. Experimental design and treatments

The schematic diagrams for the experimental design and land amendment rates are presented in Figure 8.1 and Figure 8.2. Both fields were divided into experimental plots with no buffer zone between plots and extending the full length of each field, with plot width a function of harvester operating frontage. Site 1 experimental plots were 36 m (3 harvester passes) wide with average run length 1.06 km, and Site 2 experimental plots were 24 m (2 harvester passes) wide with an average length of 0.92 km. For both fields, soil samples were taken in the centre 12 m to account for spreading variability and remove any edge effects from the fact there were not any buffers. The lack of buffers was as a result of the landholders wanting to treat the majority of their fields, therefore negotiation of field design moved toward wider treatments, rather than untreated buffer zones. Although, there was no classic buffer, we created a buffer by virtue of soil sampling in the centre of plots.

Table 8.1 Physical and chemical properties of pre-experiment soils (0–30cm depth).

Properties	***Units***	***Site 1***	***Site 2***
pH (1:5)		8.9	8.8
EC (1:5)	(dS m^{-1})	0.34	0.30
Total alkalinity (1:5)	(mg L^{-1})	207.2	157.1
SAR	(mmol$_c$ L^{-1})$^{0.5}$	1.9	4.3
CROSS	(mmol$_c$ L^{-1})$^{0.5}$	2.5	4.6
ESP	%	3.0	11.7
EDP	%	4.4	12.5
CEC	(cmol$_c$ kg^{-1})	13.9	15.4
Organic carbon	%	1.1	1.6
Chloride (Cl$^-$)	(mg L^{-1})	174	60
Nitrate (NO$_3$-N)	(mg L^{-1})	18	60
Clay content	%	29	34
Silt	%	13	16
Sand	%	58	50
Texture		Clay loam	Clay loam
Dominant clay mineralogy[‡]		Kaolinite	Kaolinite
Australian taxonomic class		Brown Dermosol	Red Dermosol
USDA soil taxonomic class		Inceptisol	Inceptisol
Location in Australia		28°58'28.7"S 150°26'49.5"E; Wariven, NSW	28°54'59.4"S 150°16'28.2"E; Eldorado, NSW

[‡] Site 1 soil has 30% Kaolinite, 15% Montmorillonite, 13% Illite/Mica and 42% Quartz, and Site 2 soil contains 34% Kaolinite, 13% Montmorillonite, and 53% Quartz.

The irrigation water was applied using centre-pivot moving irrigation machines using *in situ* groundwater from bores (Table 8.2). The centre-pivot irrigator wheel tracks passed through treatment plots uniformly. The irrigation system was designed to irrigate all plots within one day.

The Penman-Monteith (FAO56-PM) equation was used as the standard for ET$_o$ estimation. The daily ET$_o$ was predicted using the available climate data for experimental sites from the Bureau of Meteorology in Australia, with incorporation of *in situ* weather data, which was somewhat limited. The crop evapotranspiration (ET$_c$) was subsequently calculated using the crop factors (K$_c$) for cotton and wheat crops (Figure 8.3 and Figure 8.4).

Table 8.2 Selected irrigation water quality characteristics for both sites.

Sites	*pH*	*†EC (dS m^{-1})*		*Total alkalinity (mg L^{-1})*	*Chloride (mg L^{-1})*	**SAR ($mmol_c$ L^{-1})$^{0.5}$*		*Major cations ($mmol_c$ L^{-1})*			
		Mean	*SD‡*			*Mean*	*StDev*	*Na*	*K*	*Mg*	*Ca*
Site 1	8.6	1.08	±0.19	460	107	4.65	±1.25	6.83	0.41	2.72	1.55
Site 2	8.4	0.864	±0.14	410	67	17.8	±1.85	8.83	0.064	0.14	0.35

† EC is electrical conductivity, ‡ StDev is standard deviation, * SAR is sodium adsorption ratio.

Treatment applications of gypsum, lime and sulphur were applied to Site 1 experimental plots using an AgrowPlow spreader, while Site 2 had only gypsum and sulphur amendment application for the experimental period. For Site 1, four treatments with a control (no treatment) were applied with two replicates, while Site 2 had 3 treatments plus control and each treatment was applied to three replicates. Amendment application rates are presented in Figure 8.1 and Figure 8.2.

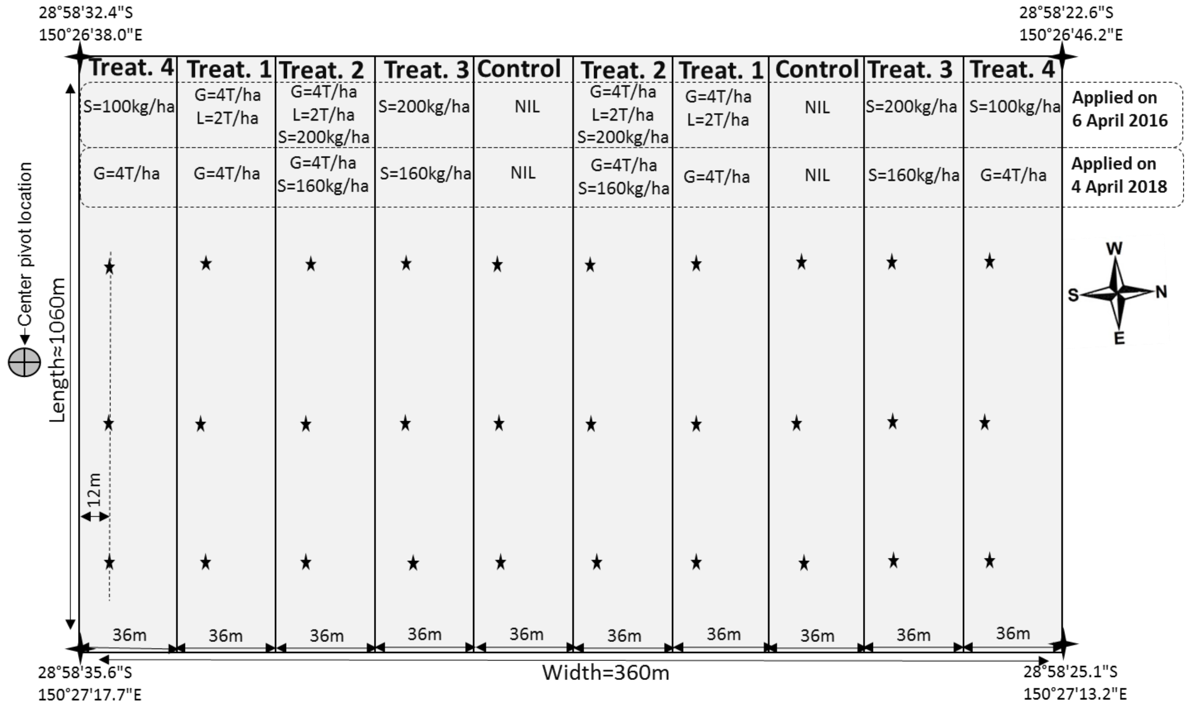

Figure 8.1 Schematic diagram of the randomized complete block design (RCBD) experiment for Site 1 treated with gypsum (G), Sulphur (S) and lime (L) and no treatment (NIL). Stars represent the soil sampling locations. Treat.x represents refers to treatment numbers where x=1, 2, 3 or 4, and C refers to control (no amendment).

Lime was applied initially in April 2016 for Site 1 to assess its ability to decrease exchangeable sodium after incorporation of applied gypsum and sulphur (Figure 8.1). Lime ($CaCO_3$) has been documented for its ability to reduce exchangeable sodium, but with limited success (McKenzie et al., 1993), principally due to its relatively lower solubility under standard conditions in comparison to the solubility of gypsum (Chan & Heenan, 1998; Greene & Ford, 1985). The combination of gypsum and lime has been used as an efficient strategy for soil structural improvement in soils with neutral pH (Bennett et al., 2014; Valzano et al., 2001), but is inefficient where soil pH is alkaline (Bennett et al., 2015a). The success of this interaction involves the dissolution of gypsum displacing hydrogen ions (H^+), increasing rhizospheric carbonic acid from plant proton output, and providing a sulphur source for microbial conversion to acid, resulting in lower pH, subsequently encouraging the potential dissolution of lime (Bennett et al., 2014). As lime can be more accessible to landholders, applying lime in the presence of an acidifying source can be more attractive, but the efficiency and cost effectiveness of this may not be, which was tested in these treatments.

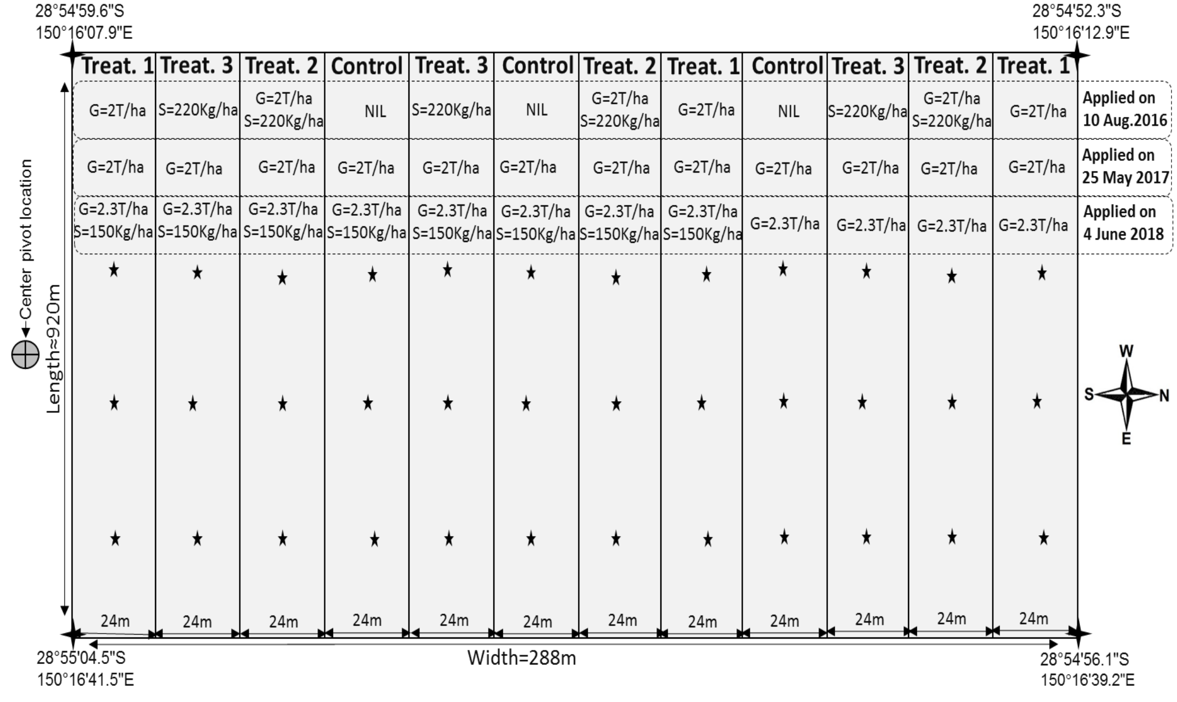

Figure 8.2 Schematic diagram of the randomized complete block design (RCBD) experiment for Site 2 treated with gypsum (G), Sulphur (S) and no treatment (NIL). Stars represent the soil sampling locations. Treat.x represents refers to treatment numbers where x=1, 2, or 3, and C refers to control (no amendment initially).

Additional amendments applied to both experimental sites during the experimentation period did not necessarily match the initial experimental design. For Site 1, lime had initially been included as a demonstration treatment on request of the grower with the thought being that use of sulphur would make the Ca from lime available. This was removed in the second season, and reverted to gypsum only. Similarly, the lower rate sulphur only treatment was removed and gypsum applied to demonstrate and investigate the use of SO_4 from the gypsum to offset the irrigation water alkalinity. For Site 1, the soil sodicity indicated no requirement for gypsum and irrigation water SAR suggested that sodium could accumulate without a sufficient leaching fraction. At Site 2 the grower applied gypsum across all treatments uniformly in the 2017 season, and then decided to compare gypsum and sulphur in the 2018 season. While these applications compromised the initial experimental design, the data is presented for the 2017 and 2018 seasons anyway, in the interest of completeness and due to the fact it does not change the ability of the research to assess HYDRUS in predicting land amendment application effects.

The soil samples were collected from treated plots from 4 increment of depths (0–10, 10–20, 20–30 and 30–40 cm) in the centre 12 m using soil cores at five different times. Site 1 soil samples were collected after about 6 months, 10 months, 12 months, 1 year & 8 months, and 2 years & 7 months from initial treatment. Site 2 treated soils were sampled after about 2 months, 6 months, 8 months, 1 year & 4 months and 2 years & 3 months after initial treatment.

8.2.3. Solute transport using HP1 model

In this study, the flow and solute transport processes for the land amendment trials were simulated using the HYDRUS-1D program (version 4.17.0140), coupled with the PHREEQC biogeochemical code (HP1) module (Jacques & Šimůnek, 2005). The measured soil chemistry of the soil profiles in question throughout time were used for comparison with the results of the HP1 model. The aim of validating the HYDRUS-1D model was to test the capability and accuracy of this model to simulate the change in soil properties ameliorated with various levels of gypsum and sulphur under application of *in situ* alkaline irrigation water and rainfall within the field. The mechanisms and components of the HP1 model, appropriate for this study, are described precisely in Jacques and Šimůnek (2005). The dual porosity van Genuchten-Mualem model was used in this study because of the difference in bulk density and porosity in the soil profile.

To simulate water movement, the initial and boundary conditions used for HYDRUS-1D were established to match the irrigation and rainfall events. A variable pressure head boundary condition was applied at the top and free drainage at the lower boundary condition. The upper concentration boundary condition was selected as a Cauchy-type boundary condition. This ensures that the concentration of applied irrigation water and rainfall at the top of soil profile depends on the concentration of ions in the solution that was applied (Leij et al., 1991; Reading et al., 2012). For the lower boundary condition, the "zero gradient boundary condition" is most appropriate for semi-infinite and infinite systems in that it assumes the concentration is continuous across the lower boundary and specifically when the flow is directed out of the modelled domain (Leij et al., 1991; Šimůnek et al., 2013). The initial pressure head of the soils was set depending on soil moisture received from the rainfall. The model's temporal and spatial discretization schemes were estimated by the Galerkin finite elements and Crank–Nicholson Scheme as described by (Šimůnek et al., 2013). A coarse grid spacing of 2 cm was used previously for HYDRUS-1D simulations (Šimůnek & Suarez, 1997), but a finer grid spacing of 1 cm was used in this case as it was more appropriate for 40 cm soil depth used. The exchangeable cations used as initial parameters in the simulations were the composition of each exchange component equilibrated with soluble ions specified for each depth (0–10, 10–20, 20–30 and 30–40 cm). The aqueous phase was able to react with the assemblage of solid phases reversibly, such as calcite ($CaCO_3$), for these alkaline soils and applied amendments.

The initial soil chemical properties were determined without incorporation of land amendments, and the solute compositions were set as the initial soil solution for each depth. The predicted solute chemistry from the initial treatment were equilibrated with the reapplied treatments for both sites. The composition of the applied *in situ* waters (i.e. irrigation and rainfall water), the soil chemical and determined hydraulic properties used in the simulations for each soil are presented in Table 8.4. The HYDRUS model was re-run for each of the individual treatment, cropping seasons and for reapplied treatments at both sites using the HP1 module. Both rainfall and irrigation water were included in the step-wise HP1 modelling process.

Since the HP1 module in the HYDRUS model does not predict the hydraulic conductivity reduction, the predicted hydraulic reduction due to alkalinity of applied water from HYDRUS model was not presented in this study

8.2.4. Geochemical modelling for land amendment using PHREEQC

Land amendment recommendations were made based upon the PHREEQC (version 3.5.0.14) model (Parkhurst & Appelo, 2013) output and provided as kilograms of amendment per mega-litre of irrigation water per hectare (Table 8.3). The required amount of elemental sulphur to neutralise the native carbonates (pedogenic carbonates) was also calculated (Table 8.5) using the HYDRUS-1D program (version 4.17.0140), coupled with the PHREEQC biogeochemical code (HP1) module (Jacques & Šimůnek, 2005).

The results associated with Table 8.3 and Table 8.5 are presented in more detail within the results section. However, it is important to note at this juncture that the amount of amendment applied to both Site 1 and Site 2 was insufficient to amend the total volume of irrigation water applied, and the free alkalinity contained within the soil. This was known at the start of the experimentation and was by landholder and researcher negotiation design. Application of the amendments attracts a significant investment on the landholder behalf. Therefore, rather than seek to fully address the potential effects of the irrigation volume, the experiment was designed to track in field observed results with desktop predicted results. The limitation of this approach was that yield and treatment efficacy cannot be directly linked.

Table 8.3 The amount of Sulphur and gypsum requirement to address the alkalinity and sodicity of applied irrigation water for Site 1 and Site 2. The PHREEQC geochemical model was used to calculate the required amendments. EC is electrical conductivity and SAR is sodium adsorption ratio. Site 1 and Site 2 received 10.2 and 5.75 ML ha^{-1} of alkaline irrigation water during the experimental period, respectively (Figure 8.3 and Figure 8.4).

Properties	*Site 1*		*Site 2*	
	Gypsum	*Sulphur*	*Gypsum*	*Sulphur*
Required in (kg ML^{-1})	---------	146.2	91.23	130.16
Required for the experimentation period (kg ha^{-1})	---------	1491.2	525	748.5
pH	7.1		7.1	
EC (dS m^{-1})	1.3		1.21	
Alkalinity (HCO_3^-) (mmol L^{-1})	0.1		0.1	
Ca (mmol L^{-1})	0.77		0.71	
Mg (mmol L^{-1})	1.36		0.07	
Na (mmol L^{-1})	6.83		8.84	
SAR (mmol_c L^{-1})$^{0.5}$	4.65		10.03	

Table 8.4 The HYDRUS model inputs used; VGM, van Genuchten-Mualem.

Parameter	*Soil 1*		*Soil 2*		
	Mean values				
Number of soil material	1		1		
Number of layers for mass balance	4		4		
Depth of soil profile (cm)	40		40		
Exchangeable cations ($cmol_c$ kg^{-1})					
Ca	8.99‡		9.99‡		
Mg	3.23‡		1.52‡		
Na	0.42‡		2.7‡		
K	1.21‡		1.19‡		
Fe	0.01‡		0.01‡		
Al	0.003‡		0.003‡		
Cation exchange capacity ($cmol_c$ kg^{-1})	13.9‡		15.41‡		
Bulk density (g cm^{-3})	1.33‡		1.29‡		
Diffusion coefficient (cm^2 min^{-1})	0.0014		0.0013		
Dispersivity (cm)	1		1		
$K_{Ca/Mg}$	2.09‡		3.07‡		
$K_{Ca/Na}$	18.37‡		8.7‡		
$K_{Ca/K}$	1.93‡		1.15‡		
Hydraulic model	VGM		VGM		
Residual water content (θ_r)	0.0377‡		0.0356‡		
Saturated water content (θ_s)	0.489‡		0.482‡		
Saturated hydraulic conductivity (cm day^{-1})	6.01‡		6.94‡		
Inverse of the air entry suction (α) (cm^{-1})	0.02†		0.021†		
Pore size distribution, n	1.16†		1.17†		
Tortuosity pore connectivity parameter (l)	0.5†		0.5†		
Grid spacing (cm)	1		1		
	Initial Treatment	2nd Treatment	Initial Treatment	2nd Treatment	3rd Treatment
Initial time step (day)	0.001	0.001	0.001	0.001	0.001
Min. time step (day)	$1x10^{-5}$	$1x10^{-5}$	$1x10^{-5}$	$1x10^{-5}$	$1x10^{-5}$
Max. time step (day)	304	620	243	220	333

‡ Measured properties for the soils used in laboratory experiments.

† Optimised properties using inverse modelling (Rosetta)

8.2.5. Agronomic practices

Cotton (*Gossypium hirsutum L.*) and wheat (*Triticum aestivum L.*) crops were planted during the experimental period. Site 1 used wheat variety Longreach Lancer LPB07-0548, and cotton variety Sicot 746B3F. The crop rotation for the experimental period was wheat, cotton, and wheat, winter, 2016, summer 2017/2018, and summer, 2018, respectively. Site 2 planted cotton in summer, 2016/2017 and wheat in winter 2017), using cotton variety Sicot 746B3F, and wheat variety Spitfire, LPB05-2148. Soils were ploughed prior to each cropping season involving surface tillage in the 0–15 cm depth. Herbicides were used at both sites to remove the influence of weeds on the plant available water and in-crop competition.

Table 8.5 The predicted effects of elemental Sulphur to reduce free alkalinity in the soil using the HYDRUS-1D program (version 4.17.0140), coupled with the PHREEQC biogeochemical code (HP1) module (Jacques & Šimůnek, 2005).

Elemental sulphur requirement (kg ha^{-1})	***Site 1***		***Site 2***	
	1042		561	
Depth (m)	**pH**	**HCO_3^- (mmol L^{-1})**	**pH**	**HCO_3^- (mmol L^{-1})**
0–0.1	6.92	2.32	7.03	2.39
0.1–0.2	6.92	2.37	6.94	2.35
0.2–0.3	6.92	2.34	6.84	2.29
0.3–0.4	6.93	2.47	6.81	2.26

8.2.6. Soil chemical analysis

Soil samples were air-dried, passed through a 2 mm sieve and analysed for chemical properties. The pH, alkalinity, EC, and soluble cations of soils were determined from soil solution extract obtained at field capacity (FC) water content (-10 kPa) based on the modified method of Bennett et al. (2016b). The FC water content was measured for each soil and depth using the hanging column method via sintered glass Buchner funnel equilibrated to -100 cm (-0.1 bar) to calculate the required volume of deionised water to obtain FC water content for each soil sample.

Thirty grams of air-dried soil was added to the calculated amount of deionised water and allowed to equilibrate for 48 hrs in 50 mL Falcon tubes at 25°C. The Falcon tubes were then centrifuged at ≈9800g for 30 minutes and the supernatant transferred to 15 mL tubes for subsequent chemical analysis. The pH and EC were then measured using a pH meter (Orion Star A111, Thermo Scientific), and EC meter (Orion Star A212, Thermo Scientific). Alkalinity was measured using a Radiometer Analytical Titrator (TIM845, Titration Manager), and the extracted soluble cations were analysed on a Perkin Elmer NexIon-ICP MS (Inductively Coupled Plasma–Mass Spectrometer). The analysed soluble cations were then used to calculate SAR using Equation 8.1.

$$SAR = \frac{[Na]}{\sqrt{0.5([Ca] + [Mg])}}$$ **Equation 8.1**

where SAR is sodium adsorption ratio $(\text{mmol}_c\ \text{L}^{-1})^{0.5}$, and square brackets indicate cation concentration $(\text{mmol}_c\ \text{L}^{-1})$.

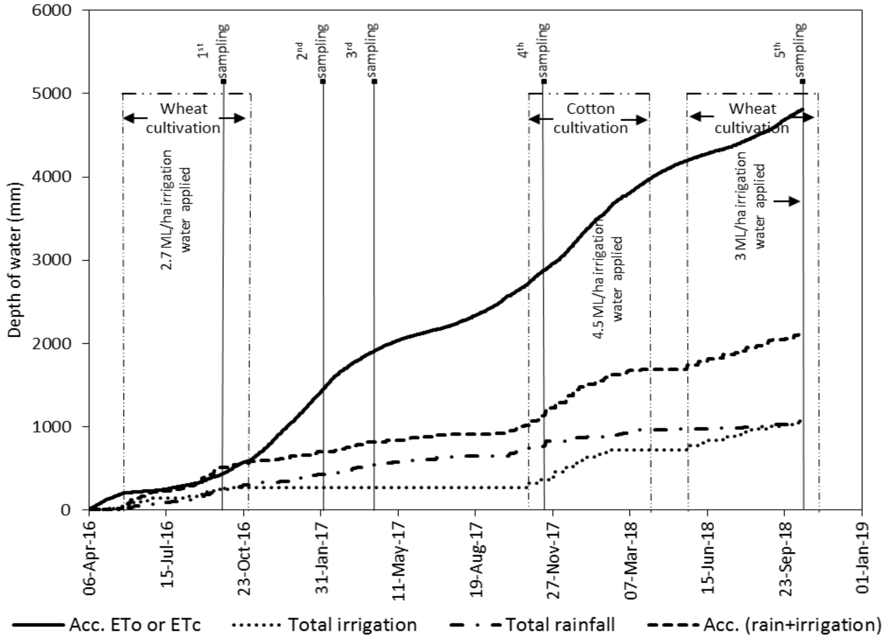

Figure 8.3 Crop cultivation duration, irrigation application, rainfall, and evapotranspiration for experimental period of Site 1.

8.2.7. Threshold electrolyte concentration (C_{TH}) analysis

To understand the expected hydraulic reduction given the land amendment approaches and the quality of the water, the soil-specific threshold electrolyte concentration (C_{TH}) was determined for each soil using the Ezlit et al. (2013) model for disaggregation prediction. The soil samples were taken prior to land amendment from both locations. The C_{TH} was measured based on the procedure of Bennett and Raine (2012b) using the mathematical model of Ezlit et al. (2013). The C_{TH} curve ($0.8rK_s$) was calculated using the function described in Ezlit et al. (2013), representing the soil solution salinity required to maintain soil saturated hydraulic conductivity at 80% (20% reduction) of the maximum saturated hydraulic conductivity for a given SAR value of irrigation water (Bennett et al., 2019a; Ezlit et al., 2013).

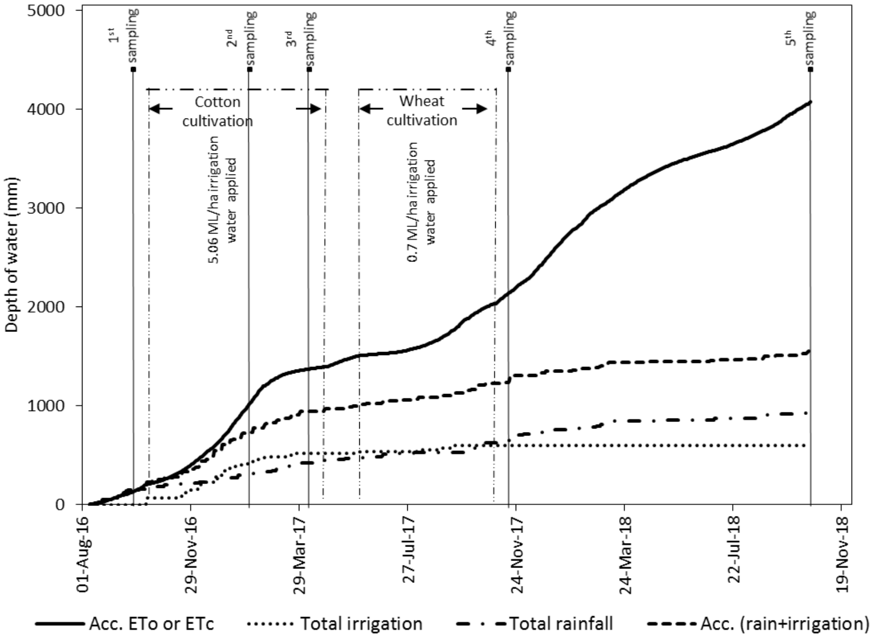

Figure 8.4 Crop cultivation duration, irrigation application, rainfall, and evapotranspiration for experimental period Site 2.

8.2.8. Cotton yield harvesting

Spatial distribution of cotton yield data was collected using a cotton picker equipped with a yield sensors and global positioning system (GPS) device. The spatial cotton yield data were collected after 2 and 2.5 years of initial treatment for Site 1 and Site 2, respectively. The cotton was harvested before reapplication of amendments occurred (harvested on 31st March 2018) for Site 1, while the cotton crop of Site 2 was harvested after reapplied treatments (harvested on 8th April 2019). The provided data from sensors needed cleaning to obtain legitimate readings, so anomalous values were removed from the main data set. This eliminated nearly all near-zero readings that were due to field-edge effects. The clean spatial data of each experimental site was entered into a GIS using the commercial GIS software Quantum GIS (QGIS v.3.6). Interpolated maps of cotton yield for both sites were prepared by krigging of the clean measurements and the boundary of amended plots selected to distinguish between plots. The VESPER program (Variogram Estimation and

Spatial Prediction with Error, developed by the Australian Centre for Precision Agriculture at the University of Sydney) was used to krige data and obtain the yield data for $2 \times 2\ m$ spacing. The raw data sets were reduced to 7747 and 4968 clean cotton yield readings measured in bale per hectare (bale ha^{-1}) for each amended plot. The yield data were then separated for each plot and statistical analysis was conducted to investigate the differences between cotton yields (Table 8.8).

8.2.9. Statistical analysis

Significant differences between soil chemical properties of amended plots were first determined by one-way ANOVA with interactions at the 95% confidence interval ($\alpha = 0.05$), unless otherwise detailed, using the Minitab V.17 statistical program. Differences between treatments where ANOVA returned significant results were investigated by performing Tukey's honest significant difference (HSD) analysis.

8.3. Results

8.3.1. Changes in pH and alkalinity after the first 12 months

The application of sulphur-alone resulted in a non-significant decrease in both pH and alkalinity. Common to all treatments, changes in pH and alkalinity were found to be significant when the soils were bare for a period of time and no irrigation water applied for both experiment sites. The application of lime in conjunction with gypsum and sulphur significantly increased the alkalinity (HCO_3^-) of the topsoil (0–0.1 m depth) of Soil 1 in the first year (Table 8.6). In general, the effect of combined gypsum and sulphur on soil pH and HCO_3^- was greater than sulphur-alone and gypsum+lime, though the change was insufficient (0.1–0.4 units of pH) for both sites. However, it can be observed that gypsum+sulphur only partially controlled the process of pH and alkalinity reduction because the pH and HCO_3^- did not significantly continue to reduce as the rate of gypsum increased. In general, the results for pH and HCO_3^- of treated plots were lower than the control (no treatment), in particular, in the surface layers (0–0.1 and 0.1–0.2 m) for both experimental sites. The exception to this was the lime+gypsum+sulphur treatments. The control treatment was different for Sites 1 and 2, where Site 2 control plots were subjected to the addition of gypsum and sulphur during experimentation by growers which resulted in compromising the experimental design.

Table 8.6 Soil solution (FC extract) pH and alkalinity (HCO_3^-; mmol L^{-1}) for Site 1 (Wariven) experimental site by the depth and through time using gypsum (ton ha^{-1}), lime (ton ha^{-1}) and sulphur (kg ha^{-1}). Data is separated by treatments and sampling period. Differing upper-case pronumerals within a specific treatment indicate significant changes due to the specific treatment over time at respective depths; Differing lower-case pronumerals within a specific sampling period represent significant treatment differences within respective depths.

Initial treats.	*Depth (m)*	*Time 1*		*Time 2*		*Time 3*		*Time 4*		*Time 5*	
		pH	*HCO_3^-*	*pH*	*HCO_3^-*	*pH*	*HCO_3^-*	*pH*	*HCO_3^-*	*pH*	*HCO_3^-*
Control (C)	0–0.1	8.30aA	5.82cA	8.19cAB	5.39aA	8.20bAB	5.03aA	8.15bB	5.98aAB	8.45bC	6.38cAB
	0.1–0.2	8.33eA	5.54aA	8.12aB	5.25bA	8.20B	4.95acA	8.25aB	6.05AB	8.41bAC	6.34bB
	0.2–0.3	8.28cA	5.05bA	8.19aA	5.37aAB	8.23A	4.86aA	8.20aA	5.89aAB	8.36aA	6.45bAB
	0.3–0.4	8.29aA	5.67aA	8.30aA	5.78aA	8.29A	5.13aAB	8.16aA	6.13aA	8.30aA	6.93acAC
G_4+L_2 (T1)	0–0.1	8.27aA	6.25aA	8.10aB	5.54aA	8.04aBC	5.20AaC	7.96aC	5.45aAB	8.10aB	4.14aC
	0.1–0.2	8.35aA	6.37aA	8.08aB	4.93aB	8.07aB	5.18aB	8.05aB	6.02aA	8.20aAB	4.79aB
	0.2–0.3	8.36aA	6.04aB	8.24aA	5.44aAB	8.19aA	4.76aA	8.15aA	6.32aB	8.18aA	5.33aAB
	0.3–0.4	8.22aA	5.92aA	8.32aA	5.84aA	8.22aA	4.81aB	8.13aA	6.47aAC	8.16aA	6.50aAB
G_4+L_2 +S_{200} (T2)	0–0.1	8.25aA	6.43aA	8.05a B	5.66aA	8.09abBC	5.20aB	7.9aD	6.55aA	8.15abC	4.54abB
	0.1–0.2	8.28bA	5.97aA	8.12aB	5.40bA	8.16aBC	5.13aA	8.12aC	6.18aA	8.32abA	5.03aA
	0.2–0.3	8.20bA	6.22aA	8.19aA	5.19aA	8.19aA	4.71aAB	8.16aA	6.52aAC	8.21aA	5.33aA
	0.3–0.4	8.21aA	6.08aA	8.26aA	5.34aA	8.25aA	4.90aAB	8.13aA	6.82aAC	8.24aA	6.27abA
S_{200} (T3)	0–0.1	8.25aA	5.13bA	7.95abB	5.37aA	8.15abAB	4.69aAB	7.93aB	5.78aAC	8.23aAC	5.27bA
	0.1–0.2	8.26cA	5.90aA	8.16aA	5.40bAB	8.15aA	4.36bcB	8.16aA	5.55aAC	8.36bA	5.85abC
	0.2–0.3	8.25cA	5.27bA	8.19aAB	5.57aA	8.14aB	4.56aAB	8.20aAB	5.82aAC	8.32aC	6.50bC
	0.3–0.4	8.19aA	5.45aA	8.24aAB	5.53aA	8.12aA	4.76aA	8.12aA	5.78aAB	8.28aB	6.62aB
S_{100} (T4)	0–0.1	8.13bA	5.23bA	7.97abB	5.30aA	8.08abAC	4.95aA	7.94aB	5.64aA	8.20aAD	5.32bcA
	0.1–0.2	8.21dA	5.68aA	8.13aA	5.45bA	8.08aA	4.73abB	8.15aA	5.73aAC	8.25abB	5.84abAC
	0.2–0.3	8.28cA	4.72bA	8.16aA	5.42aA	8.16aA	5.12aA	8.25aA	5.75aA	8.28aA	6.01abA
	0.3–0.4	8.23aA	5.47aA	8.26aA	5.43aA	8.16aA	5.06aA	8.20A	6.25aA	8.17aA	6.50aA

8.3.2. Changes in pH and alkalinity after treatment reapplication (Years 2 and 3)

Changes in pH and HCO_3^- were found to be significant for all treatments in comparison to the control for both soils (Table 8.6 and Table 8.7). The additional application of gypsum and sulphur resulted in significantly lower alkalinity and pH, particularly within surface layers (0–0.1 and 0.1–0.2 m) for both experimental sites. The increase of pH and HCO_3^- in the control was significant ($P<0.001$) compared to initial soil sampling for both sites, and was a function of irrigation water application. The magnitude of reduction in pH and HCO_3^- was significantly lower for all treatments in comparison to the control for year 2 and 3, as compared to year 1. The reapplication of gypsum and sulphur, in treatments where initially lime combined with gypsum and sulphur had been applied, exhibited a significant decrease in the HCO_3^- and non-significant decrease in the pH within the 0–0.1 m and 0.1–0.2 m layers for Site 1, as compared to all other treatments (Table 8.6).

At Site 2, the major decrease in the soil solution pH and HCO_3^- occurred due to reapplication of amendments, with a lower amount of applied irrigation water during year 2 and 3. Reduction in pH and HCO_3^- was greater for all treatments than the control because the control received a lower rate of amendment during experimental time (Site 2 control plot was subjected to application of gypsum and sulphur during experimentation; see Figure 8.2). However, there were significant differences in pH and HCO_3^- for subsoil depths (0.2–0.3 m and 0.3–0.4 m) in comparison to the initial soil solution of Site 2.

Table 8.7 Soil solution (FC extract) pH and alkalinity (HCO_3^-; mmol$_c$ L^{-1}) for Site 2 (Eldorado) experimental site by the depth and through time using gypsum (ton ha^{-1}) and Sulphur (kg ha^{-1}). Data is separated by treatments and sampling period. Differing upper-case pronumerals within a specific treatment indicate significant changes due to the specific treatment over time at respective depths; Differing lower-case pronumerals within a specific sampling period represent significant treatment differences at respective depths.

Initial treats.	*Depth (m)*	*Time 1*		*Time 2*		*Time 3*		*Time 4*		*Time 5*	
		pH	*HCO$_3^-$*	*pH*	*HCO$_3^-$*	*pH*	*HCO$_3^-$*	*pH*	*HCO$_3^-$*	*pH*	*HCO$_3^-$*
Control (C)	0–0.1	8.35cdA	5.26bA	8.35bA	6.56aB	8.61bB	6.54abB	8.17acA	4.87aB	8.07bC	3.12aC
	0.1–0.2	8.38aA	5.31acA	8.18aBDE	6.19aB	8.53bC	6.96bB	8.21aD	4.05aC	8.15aE	2.91aD
	0.2–0.3	8.42cA	5.58bA	8.12aB	5.94abA	8.46aAC	5.94aA	8.21aBC	4.55acB	8.28aC	2.82aC
	0.3–0.4	8.38bA	6.02cA	8.23aA	5.95aAB	8.39aA	6.43bA	8.14aA	4.92bB	8.33aA	2.60aC
G$_2$ (T1)	0–0.1	8.19aA	5.19aA	8.18aA	5.89aA	8.38aB	5.69abAB	7.97aC	4.51aAC	7.95aCD	2.76aD
	0.1–0.2	8.36aA	6.11aA	8.19BaCD	6.15aAB	8.41aA	5.14aC	8.17aC	3.84aD	8.08aD	2.62aE
	0.2–0.3	8.31aA	5.11aA	8.19aB	5.86aAB	8.43aC	5.19aAB	8.24aAB	4.16aAC	8.28aAB	2.62aD
	0.3–0.4	8.28aA	5.12aA	8.23aA	6.29aA	8.33aA	5.17aA	8.14aA	3.20aB	8.27aA	2.52aB
G$_2$+S$_{220}$ (T2)	0–0.1	8.09bA	4.73aA	8.30bB	6.38aB	8.38aBC	5.46acA	7.92abD	4.81aA	8.00abAD	3.01aC
	0.1–0.2	8.22bA	4.97bA	8.27aA	6.32aA	8.45abB	6.48bAB	8.17aAC	4.33aAC	8.09aAD	2.62aBC
	0.2–0.3	8.24abA	5.08aA	8.20aA	5.48bA	8.38aAB	5.57aA	8.20aAC	4.01abB	8.27aA	2.48aC
	0.3–0.4	8.23aA	5.35aA	8.27aAB	5.67aA	8.35aB	5.74abaA	8.15aAC	3.94aB	8.29aAB	2.51aC
S$_{200}$ (T3)	0–0.1	8.31cA	5.26aA	8.36bA	6.51aB	8.46abA	5.73abAB	7.88abBC	4.25aC	7.93aBC	2.71aD
	0.1–0.2	8.41acA	5.31bA	8.29aAB	6.32aB	8.48abAB	5.98aBC	8.21aAC	4.44aD	8.13aBC	2.55aE
	0.2–0.3	8.37acA	5.58abA	8.33bAB	5.71aA	8.39aA	5.93aA	8.17aB	3.10abB	8.29aAB	2.54aC
	0.3–0.4	8.32acA	6.02bA	8.30aA	5.88aA	8.37aA	5.49aA	8.13aB	3.37abB	8.27aA	2.46aC

8.3.3. Treatment effect on soil solution salinity and sodicity with time

Application of gypsum increased the electrolyte concentration and concentration of Ca^{2+}, which resulted in lowering of the SAR within the 0–0.1 and 0.1–0.2 m depths in both soils. This trend was more apparent for Site 2, which initially had lower EC and higher SAR, with a lower rate of irrigation water applied. Application of lime in combination with gypsum and sulphur resulted in a non-significant minor increase in EC and did not reduce SAR values further in comparison to the gypsum and lime combination treatment. The changes in EC and SAR for the application of sulphur-alone were also not found to be significant compared to the control at any time at either of the two experimental sites. For the subsoil depths (0.2–0.4m depth increments) of both soils, EC and SAR were slightly altered, but the change was non-significant in comparison to the control and between amended plots for all measurements. A slight increasing in salinity was observed at the lower depth of soil profile (0.2–0.4m), due to redistribution of salts, downward flux of salts and/or lateral salt movement after 1 year of initial amendment application (Figure 8.5 and Figure 8.7). The SAR reduction was more visible for the topsoil with maintained SAR of the lower depths (i.e. 0.2–0.4m) (Figure 8.6 and Figure 8.8).

The trend for increased reduction of salinity and SAR was more pronounced with the second application of gypsum at Site 1. The same trend was apparent for Site 2, especially after the second and third application at the 0–0.1 and 0.1–0.2 m depths for gypsum applied plots.

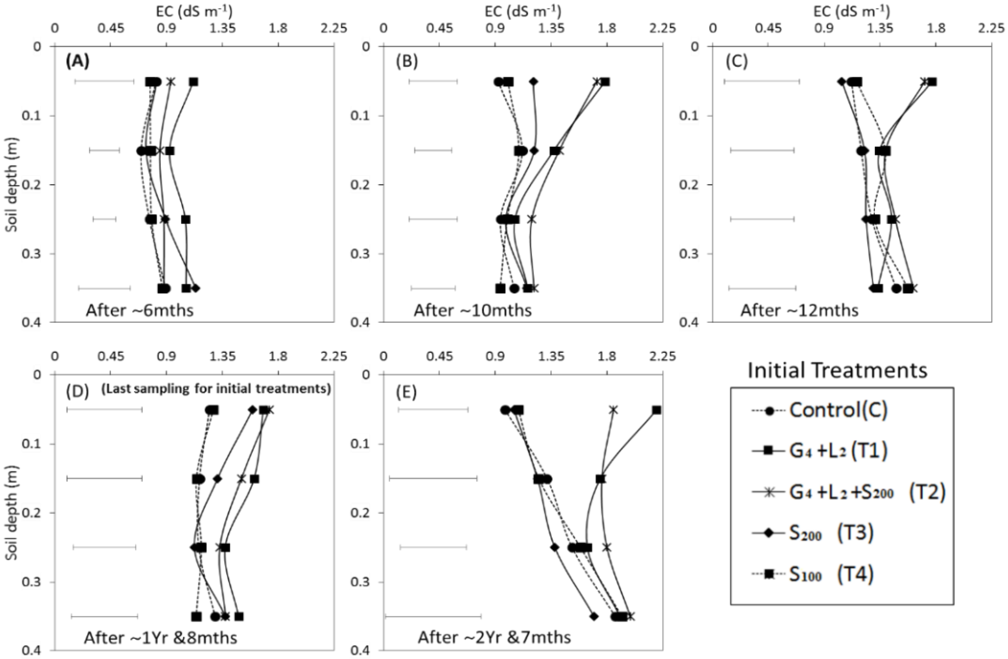

Figure 8.5 Soil solution electrical conductivity (EC) at field capacity for amended plots of Site 1 measured in Time 1(A), Time 2 (B), Time 3 (C), Time 4 (D) and Time 5 (E) soil sampling periods. Bars indicate Tukey's honest significant difference values (α=0.05) between treatments within respective sampling.

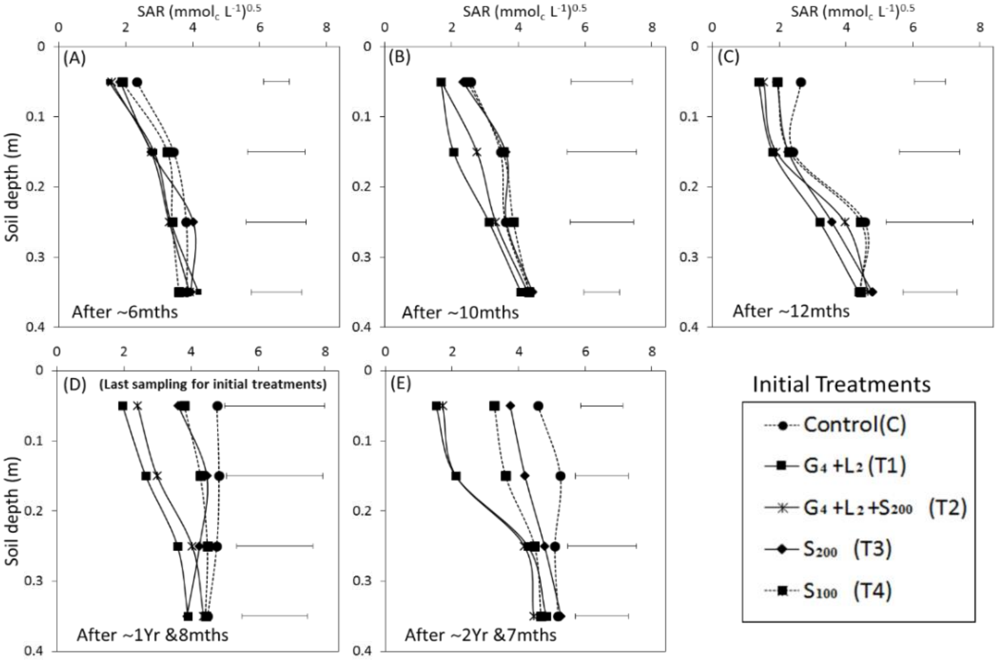

Figure 8.6 Soil solution sodium adsorption ratio (SAR) at field capacity for amended plots of Site 1 measured in Time 1(A), Time 2 (B), Time 3 (C), Time 4 (D) and Time 5 (E) soil sampling periods. Bars indicate Tukey's honest significant difference values (α=0.05) between treatments within respective sampling.

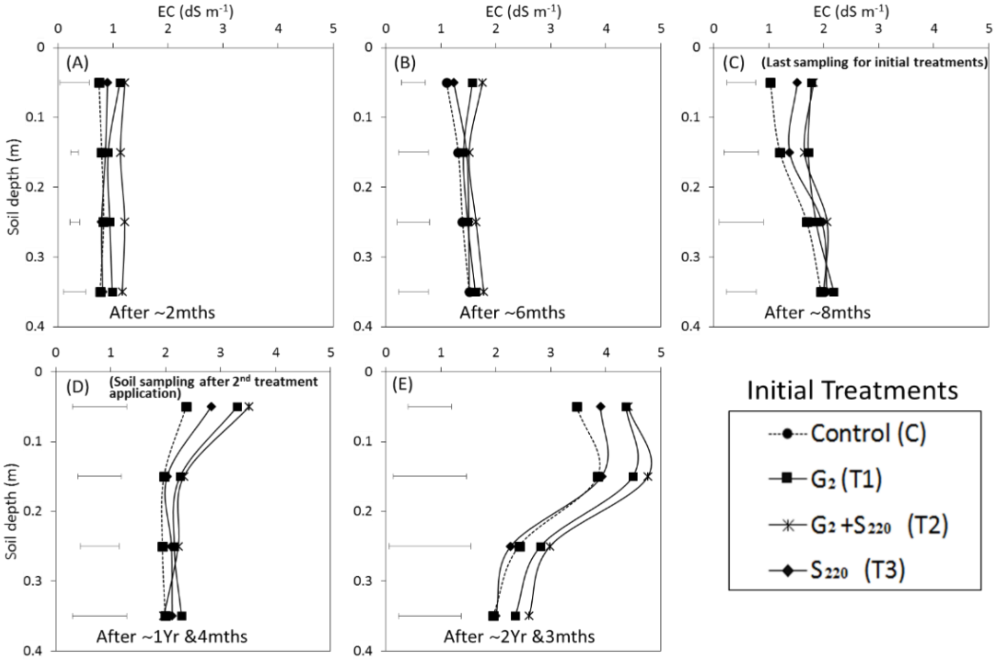

Figure 8.7 Soil solution electrical conductivity (EC) at field capacity for amended plots of Site 2 measured in Time 1(A), Time2 (B), Time 3 (C), Time 4 (D) and Time 5 (E) soil sampling periods. Bars indicate Tukey's honest significant difference values (α=0.05) between treatments within respective sampling.

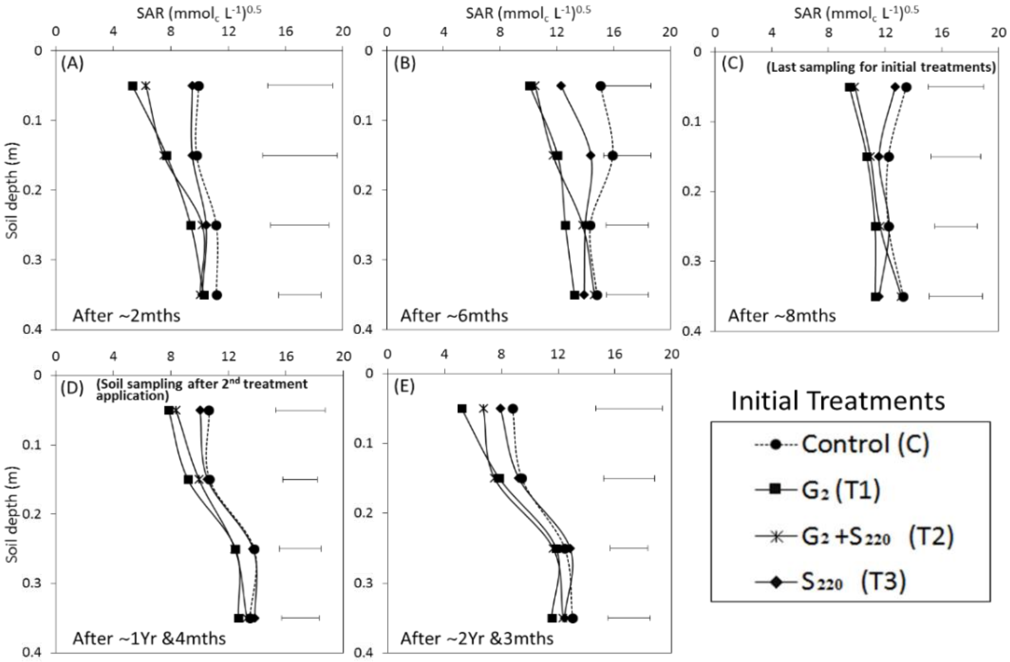

Figure 8.8 Soil solution sodium adsorption ratio (SAR) at field capacity for amended plots of Site 2 measured in Time 1 (A), Time 2 (B), Time 3 (C), Time 4 (D)and Time 5 (E) soil sampling periods. Bars indicate Tukey's honest significant difference values (α=0.05) between treatments within the respective sampling.

8.3.4. Amendment effects on solute chemistry changes using geochemical modelling

The HP1 modelling outcomes for pH, alkalinity, EC and SAR for both soils are presented in Figure 8.9 and Figure 8.10. In general, the HP1 model did not effectively predict the pH and HCO_3^- soil chemistry changes for predicted land amendment, compared to the observed results, over the 27 months period. The predicted results indicated that HP1 model over predicted the pH and under predicted the alkalinity, with predictions significantly different from the observed results for both sites; the alkalinity of Site 2 was reasonably predicted. The EC and SAR were predicted relatively with a good agreement of the predicted with the observed values. Although there was some limitation in the prediction of EC and SAR by HP1 model, the predicted results were not significantly different from the observed results of the field amendment. The predicted solute chemistry changes in Site 2 were in greater agreement with observed results compared to Site 1 simulated by HP1 model, which is potentially due to the difference in the lower amount of alkalinity application and treatment rates.

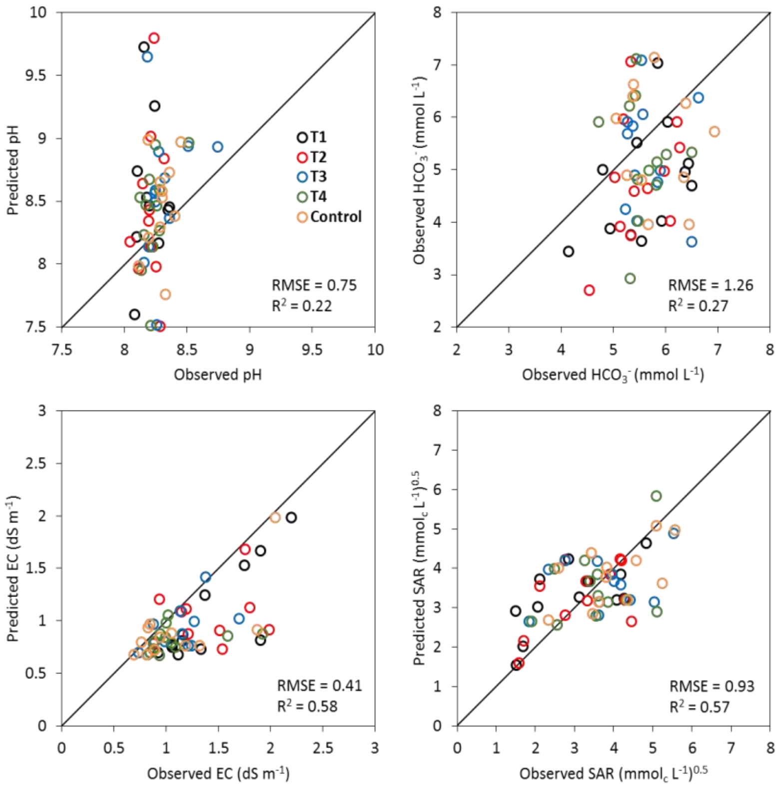

Figure 8.9 The relationship between observed and HYDRUS predicted results of pH, alkalinity (HCO_3^-), electrical conductivity (EC) and sodium adsorption ratio (SAR) for Site 1. The diagonal solid line represents the y=x line. RMSE is the root mean square error, and *R^2* is the coefficient of determination where predicted values fitted to y=x line.

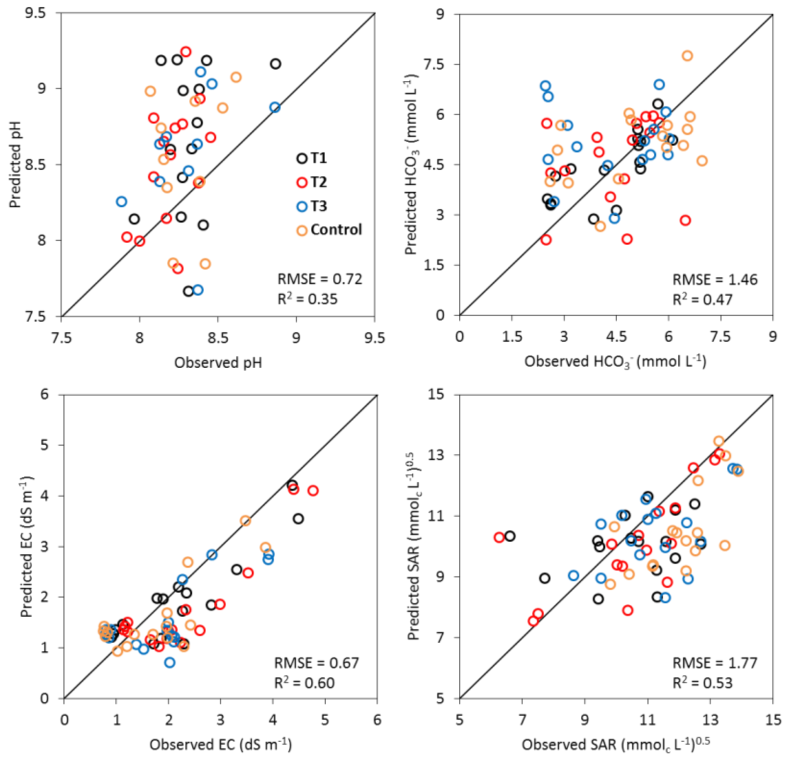

Figure 8.10 The relationship between observed and HYDRUS predicted results of pH, alkalinity (HCO_3^-), electrical conductivity (EC) and sodium adsorption ratio (SAR) for Site 2. The diagonal solid line represents the y=x line. RMSE is the root mean square error, and R^2 is the coefficient of determination where predicted values fitted to y=x line.

8.3.5. Amendment requirement for the alkalinity of irrigation water and soil using PHREEQC and HP1 geochemical modelling

The predicted results of the PHREEQC model for amendment requirement in offsetting alkalinity of the current irrigation water demonstrated that the alkaline irrigation water of Site 1 and Site 2 require 146.2 and 130.16 kg ML^{-1} of elemental sulphur in order to attain pH=7.1 and alkalinity 0.1 (mmol L^{-1}) (Table 8.5). The modelling results also demonstrated that 91.23 kg ML^{-1} of gypsum is required for Site 2 irrigation water to lower SAR from 17.8 to 10.03 SAR $(mmol_c\ L^{-1})^{0.5}$, and no gypsum is required for Site 1 irrigation water due to its low sodicity (Table 8.5 and Table 8.2). The existing free alkalinity in the soil is expected to confound the land amendment irrigation requirement because some of the applied amendments are likely to interact with the existing alkalinity in the soil. The predicted results for free alkalinity neutralisation using the HP1 module demonstrated that soils required 1042 and 561 kg ha^{-1} of elemental sulphur to neutralise the free alkalinity and address the soil buffering capacity to reduce pH to ~7 for Site 1 and 2, respectively (Table 8.5). The required elemental sulphur to neutralise the free alkalinity in the soil profile was not addressed by the applied amendments in this study, and the applied amendments were insufficient to address the total volume of irrigation water applied, but did provide a data set for comparison of field operations and their observed results with predicted results.

8.3.6. Soil solution dynamics and the threshold electrolyte concentration (C_{TH})

Based on threshold electrolyte concentration (C_{TH}) analysis, the irrigation water quality would be expected to result in a K_s reduction of ~8 and 58% for Sites 1 and 2, respectively (Figure 8.11). Although, the expected K_s reduction was 58% with application of *in situ* irrigation water quality for Site 2, the control (no treatment) only presented ~35% reduction in K_s. A notable decrease in K_s reduction would be expected where gypsum was applied to both soils. The application of gypsum in combination with lime and/or sulphur increased the EC of solutions and decreased the SAR values of the soil solution, resulting in K_s improvement. Although the application of amendments (Site 1) caused slightly increased reduction in EC and SAR, the effectiveness is suggested to provide little improvement in K_s in terms of the laboratory based C_{TH} analysis, indicating this site already has undergone equilibrium with irrigation water quality. Figure 8.11 shows that the application of lime+gypsum (T1) and lime+gypsum+sulphur (T2) would be expected to improve the soil hydraulic conductivity by only ~1–1.5% K_s reduction for Site 1 in the first year and year 2 and 3. Meanwhile, the application of gypsum-alone (T1) and gypsum+sulphur (T2) decreased K_s reduction from 58% to only ~10% reduction after 8 months of treatment and ~5–3% K_s reduction for the year 2 and 3 for Site 2.

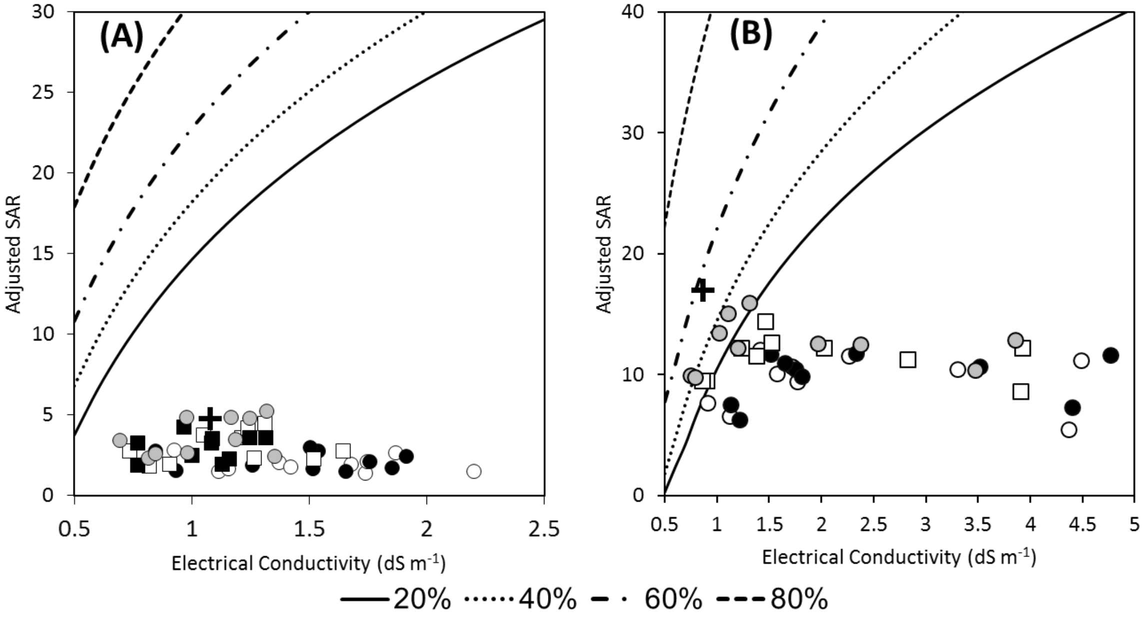

Figure 8.11 Threshold electrolyte concentration curves for Site 1 (A) and Site 2 (B) with adjusted sodium adsorption ratio for the remaining alkalinity and soil solution concentration. Soil solution at field capacity for 0–10 and 10–20 m depths, 20–40 m data were ignored as there was an overall non-significant difference between treatments for these depths. Both soils sampled for amended plots with Treatment 1 (white circles), Treatment 2 (black circle), Treatment 3 (white squares), Treatment 4 (black squares) and control (grey circle). Percentages indicate the percent reduction in hydraulic conductivity expected for any water quality "x,y". The plus symbol indicates the percentage of hydraulic conductivity reduction predicted for applied irrigation water quality.

8.3.7. Crop yield

The spatial distribution of cotton yield is presented in Figure 8.12 and the statistical analysis for finding differences between amended plots are shown in Table 8.8. In general, the yield results clearly indicate that both experimental sites were largely affected by low irrigation distribution uniformity of the centre pivots installed at both paddocks. Also, spatial yield maps indicate that the yield was affected by wheel tracks for both pivots, with this effect more evident at Site 1. For Site 1, the application of gypsum+lime+sulphur resulted in the highest yield, which was significantly higher than the sulphur-alone application and control. At Site 2, the initial sulphur-alone treatment (T3) produced the highest cotton yield (8.965 bale ha^{-1}) and the lowest yield was for initial gypsum-alone plots (T1) (8.751 bale ha^{-1}) (Table 8.8), where both treatments where ended up with application of gypsum 2.3 (T ha^{-1}) in 2017 and 2.3 (T ha^{-1})+sulphur (150 kg ha^{-1}) in 2018.

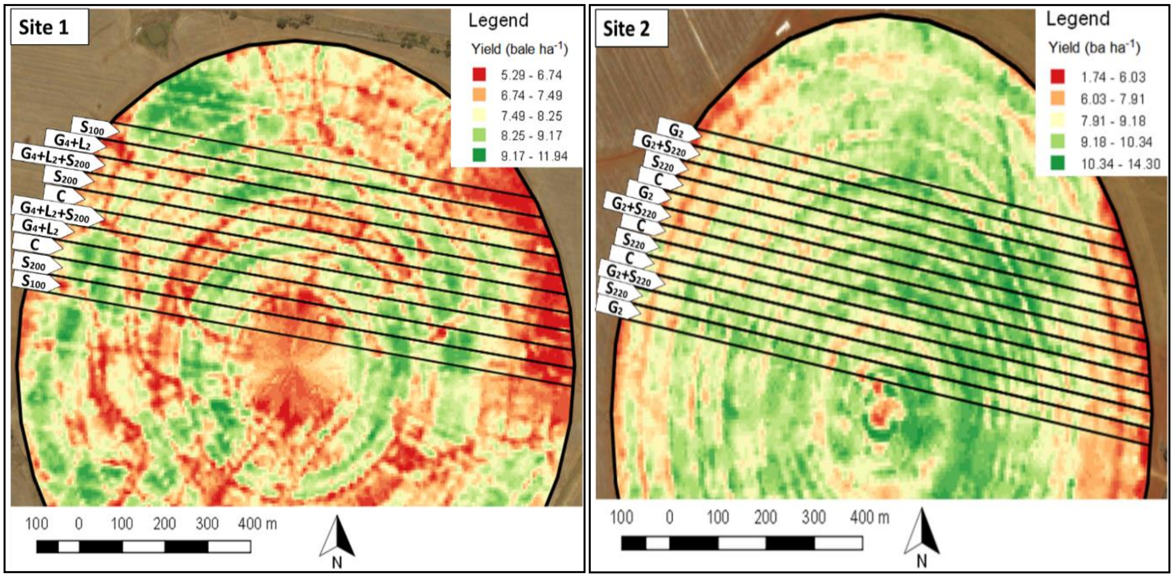

Figure 8.12 Spatial distribution of cotton yield (bale ha^{-1}) after 2 and 2.5 years from initial treatment for Site 1 and Site 2, respectively.

Table 8.8 Statistical analysis for the yield data shown in Figure 8.12. StDev represents the standard deviation of the yield for each of plots, Adj.MSE is adjusted mean square error and n is number of cotton yield (bale ha^{-1}) readings for the amended plots.

			Site 1				
Initial Treatments	*Mean (bale ha^{-1})*	*StDev*	*95% Confidence Interval*		*Adj. MSE*	*F-Value*	*P_{value}*
Control	7.637c	0.874	7.620	7.654	0.582	57.47	<0.001
G_4+L_2	7.768a	0.743	7.751	7.785			
G_4+L_2+S_{200}	7.769ab	0.662	7.752	7.786			
S_{200}	7.735b	0.693	7.719	7.752			
S_{100}	7.643c	0.823	7.626	7.66			
			Site 2				
Control	8.768ab	1.492	8.73	8.807	1.906	24.59	<0.001
G_2	8.751a	1.463	8.713	8.789			
G_2+S_{220}	8.826b	1.2632	8.788	8.864			
S_{220}	8.965c	1.29	8.927	9.004			

8.4. Discussion

8.4.1. Efficacy of land amendment approaches in ameliorating irrigation water effects

The amendments chosen in this study have considerably improved the soil chemistry but through different mechanisms. The results of this study clearly demonstrated that gypsum-alone or gypsum+sulphur have potential efficacy to reduce deleterious effects of sodic and alkaline groundwater when applied to both lands, which supports recent findings in the coal seam gas industry (Ali et al., 2018; Bennett et al., 2016b; Johnston et al., 2013). Gypsum resulted in decreased sodicity of soils and reduction in the applied irrigation water SAR, with increase in the electrical conductivity of the soil solutions also apparent following amendment application. This process is expected to result in the increasing ionic strength which further leads to a reduction in soil pH and clay dispersion within the soil system (Chorom & Rengasamy, 1997). The addition of sulphur addressed the residual alkalinity in the soil, existing from numerous years of historical irrigation without amendment, and the alkalinity in the irrigation water. The fact that the sulphur was converted to an acidifying substance indicates the presence of *Thiobacillus thiooxidans* bacteria (Suzuki et al., 1999). Where gypsum+sulphur was applied, both the SAR and alkalinity were addressed simultaneously, but the extent of the effect did vary.

Land amendments provide a potential solution for the strategic utilisation of groundwater sources, such as alkaline and sodic CSG water, or other marginal artesian waters in Australia (Bennett et al., 2016b), thereby allowing the beneficial use of alkaline and sodic groundwater for irrigation purpose. In this study, the alkalinity of the applied irrigation water was neutralised particularly for topsoil from the formation of acidity from sulphates (gypsum and sulphur) with contribution of microbial processes (Germida & Janzen, 1993), or through the leaching of alkaline ions (Rengasamy & Olsson, 1991; Wallace, 1994), whereas the addition of a soluble Ca source (gypsum) reduced the SAR of the soil solution. However, the oxidation of sulphur is a slow biological process (Gupta & Abrol, 1990), and also depends on climate conditions (Germida & Janzen, 1993). Increasing calcium in the soil system is most commonly achieved by the application of gypsum (Amezketa et al., 2005; Rengasamy & Olsson, 1991) and lime (McKenzie et al., 1993). However, the application of lime+gypsum resulted in maintaining high alkalinity in comparison to other treatments. This trend is expected to be due to the precipitation of calcium in the soil system buffered with high alkalinity and pH (Barrow, 1982), and insufficient leaching processes (Shainberg & Gal, 1982). Chorom and Rengasamy (1997) and Bennett et al. (2015a) indicated that lime has low solubility at high pH values, and it cannot be expected to provide adequate calcium in the soil solution to combat sodicity. In addition, the presence of lime in the soil system may be expected to substantially reduce the gypsum solubility through coating surrounding gypsum particles, resulting in reducing gypsum surface area in contact with the solution (Keren & Kauschansky, 1981). Our data endorse that the pH of the soils must be reduced before application of lime, even where applied with gypsum.

For both of the experimental sites, the application of gypsum-alone and gypsum+lime+sulphur reduced SAR for the duration of the experiment, with the results more evident for treatments plots with a subsequent additional application of gypsum. The change in EC and soluble cations were greater for the topsoil (0–0.1) and extended to 0.1–0.2 m in the longer term, although influence was less evident in the lower depths, due to a lack of leaching during rainfall events and irrigation cycles. In 2016, the difference between the crop based evapotranspiration demand and the combined rainfall and irrigation applications suggested only a small deficit, although from 2017 onwards the crop water requirement went into significant deficit (Figure 8.3 and Figure 8.4). On this basis, it is clear that a sufficient leaching fraction did not exist (Shaw & Thorburn, 1985), resulting in salt storage towards the surface, which was similarly observed in the work of Bennett et al. (2016b). This trend was more evident for Site 2, which initially had low EC and higher SAR values, and was subject to a lower rate of irrigation water applied throughout the experimental period. The increase in EC appeared to coincide with a reduction trend in SAR. This trend only partially controls the process because the SAR did not continue to reduce and the EC increased as the rate of gypsum increased. This was most likely due to insufficient leaching, but would be also dependent on the field redox conditions.

The net effect of gypsum is expected to be a reduction in ESP and SAR of soils over the long-term (Ellington et al., 1997), with the EC of solution reduced after the initial application (Bennett et al., 2015a; Valzano et al., 2001), due to cation exchange of sodium with calcium, and subsequent leaching of cations and anions. The results of the current work support this, and are further consistent with the outcomes of Ellington et al. (1997) and Bennett et al. (2014) who indicated that SAR and or ESP, as well as concomitant clay dispersion, were lowered after gypsum application on Red-Brown Earths (Chromosols and Sodosols) for dryland cropping. The results also confirmed that the sulphur effects are more apparent in the combination with gypsum or gypsum+lime to enhance desirable soil chemistry. However, the applications of amendments resulted in an insignificant decrease of pH within the soil profile, while a gypsum-sulphur combination caused the greatest reduction in pH. This is of concern for practical management of land reclamation. It can be hypothesised that residual alkalinity has a major role in buffering soil system, resulting in maintaining soil alkalinity. The application of sulphur was primarily added to address the alkalinity in the irrigation water without addressing the existing residual alkalinity in the soil. The HP1 modelling demonstrated that these soils required 1042 and 561 kg ha^{-1} of elemental sulphur to contest the soil free alkalinity and reduce pH to ~7 for Site 1 and 2, respectively. Moreover, the geochemical modelling showed that the pH of irrigation water was higher than 8, with alkalinity (HCO_3^-) of < 1.46 mmol L^{-1} for the application gypsum and sulphur combination for both sites. The modelling results also indicates that the applied amount of sulphur alone was unable to reduce alkalinity and pH sufficiently, and this is consistent with the results observed for the initial treatments. The reapplication of amendments and change in treatments caused a limitation in the conclusion of the finding of this work within the context of amendment efficacy, in particular for Site 2, so further discussion cannot be had without undue speculation. Therefore, there remains a requirement to develop further field-based amendment efficacy experiments.

8.4.2. Use of HP1 for modelling and planning land amendment strategies

The predicted results indicate that the HP1 model was not adequately able to simulate the changes in pH and the alkalinity for the amended alkaline soils, as compared to observed results, in the field under alkaline irrigation. In general, the HP1 model over predicted the pH and under predicted the HCO_3^- for amended lands. This simulation tendency indicates that the HP1 model logic is functioning correctly. Lindsay (1979) indicated that the HCO_3^- concentration is at its maximum at pH of 8.3, the concentration of HCO_3^- is expected to deplete with increasing the concentration of carbonates for pH >8.3, but survive in soil solution until approximate pH of 12. The HP1 model over predicted the soil solution pH ~8.2–9.75 whereas the maximum observed pH was ~8–8.5 for both soils. It is also important to note that the carbonate proportions increase at a rate 10 times faster than bicarbonates per unit increase in soil pH (Brady & Weil, 2008; Lindsay, 1979). In addition, the chemistry of the soil solution is different when affected with increasing carbonate precipitation such as cation and anion exchange and complex formation, dissolution and precipitation of the ionic species for pH above 8.5 (Abrol et al., 1988; Bohn et al., 2015; Rengasamy, 2016). These complex processes likely affect the soil solution chemistry that occurred in the soil, explaining the over prediction of pH, and highlighting that while HP1 provides a reasonable tool for investigating scenarios, the lack of exchange phases behaving as soil minerals is a shortcoming that is important in this particular case.

The over prediction of pH by the model is probably affected by the limitation of partial CO_2 pressure in the soil predicted by the model compared to the field. Mashhady and Rowell (1978) and Loeppert (1986) indicated that the main factors responsible for alkaline pH are the partial CO_2 pressure and carbonate ions. Moreover, there are many sources that are involved in the variation of $[H^+]$/pH in the soil and ignored by the model, such as carbon dioxide from the atmosphere or from microbial respiration (Koizumi et al., 1991). Carbon dioxide, when dissolved in water, produces carbonic acid (Berner, 1992; Brady & Carroll, 1994). The chemical composition of rainwater varies spatially and temporarily (Ayers & Gillett, 1984; Vet et al., 2014), depending on the gaseous composition of the atmosphere. Nitrogen and sulphur oxides released from industrial activity can increase the acidity of rainwater and subsequently acidify the soil — not a likely mechanism in this case, but of consideration globally. Rengasamy (2016) discussed that soil pH is largely controlled by the concentration of CO_2 in the soil solution, in addition to the presence of carbonates and bicarbonates. While the concentration of CO_2 in the atmosphere is about 0.0035%, it can increase in soils through biological processes and activities up to 0.5% (Rengasamy, 2016; Williams et al., 2018). Furthermore, plant roots usually exude acids into soils as part of their natural metabolisms as well as their contribution in root-induced pH changes through releasing charges (H^+) to compensate for an unbalanced cation or anion uptake at the soil root interface (Hinsinger et al., 2003). Hence, a model may need to account for variation in these complex activities responsible for variation in the pH and HCO_3^- within the soils in order to better predict alkalinity and pH dynamics.

The predicted EC and SAR outcomes were also in a reasonable agreement with observed results within the field, but could certainly be improved by the inclusion of complex factors discussed above for pH and HCO_3^- that would also be expected to affect the electrolyte concentration and ionic composition of the soil solution. The difference in evaporation/evapotranspiration in the field and the equilibrium chemical reactions and other complex processes potentially also have a major role in the strength of the correlation between predicted and observed results for EC and SAR values.

The overall predicted results indicate that the HP1 model could be considered as a conservative model that would likely ensure that environmental degradation was minimised from a soil structural point of view. However, results for pH and HCO_3^- such as those obtained in this work could lead to over application of sulphur based products, which would have financial ramifications for landholders and potentially result in acidification of the field environment where it was not expected. Therefore, it is prudent that if using HP1 for land amendment planning in its current state that these limitations are presented as caveats to the modelled output. Given the fact that most of the model parameters are based on the laboratory experiment, it is imperative to work towards land planning models capable of including continuous proxy data streams that may help infer some of the complexity in precipitation/dissolution dynamics and the associated changes in soil structural condition.

8.4.3. The importance of buffering and leaching on ameliorative effect

In the limited leaching environments of arid and semi-arid regions, native calcite is a common mineral in the soil, and the pH can vary between 8 to 10 (Essington, 2015; Pal et al., 2000). Both soils of Wariven and Eldorado in NSW contained native calcium carbonate (pedogenic) and/or derived from the application of alkaline water received in previous years prior to this study. The presence of free alkalinity in these soils can be expected to affect the amendment required to address the alkalinity within the soil profile, and is difficult to account for in terms of an elemental sulphur recommendation. An accurate recommendation to offset the native alkalinity needs a precise potential laboratory analysis.

The low dissolution of calcium carbonates is usually a limiting factor in lowering alkalinity as well as their contribution to lower the sodicity (Keren & Kauschansky, 1981; Nadler et al., 1996). The results of this study and previous studies suggest that an external source of calcium (i.e. gypsum) and sulphur applied to alkaline soils can increase the dissolution of pedogenic carbonates, resulting in alkalinity reduction (Bennett et al., 2015a; Gupta et al., 1984; Pal et al., 2000).

The HP1 modelling results confirmed that the application of elemental sulphur is able to dissolve the existing carbonates (pedogenic carbonates) in the soil. These results suggest that the soils require elemental sulphur application prior to the application of amendments for offsetting the alkalinity of irrigation water. It can be perceived that some of the applied amendments might contribute in ameliorating the existing alkalinity in the soil profile. However, the initial application of neutralising materials (e.g. elemental sulphur) was required to neutralise the existing pedogenic carbonates prior to using the land amendment irrigation strategy. The presence of soil carbonates would also be expected to affect the solubility of gypsum through coating gypsum particles (Keren & Kauschansky, 1981). These outcomes suggest that neutralising alkalinity is feasible through application of acid-forming materials to soils, there remains a challenge of accumulation of salts and increasing ionic osmotic potential in the soil solution.

Our results clearly demonstrate that alkaline irrigation water can be utilised, but there remains a requirement for an adequate leaching fraction to be developed. In essence, the leaching process in the arid and semi-arid lands is usually less effective due to limitation of rainfall and a large amount of applied irrigation water involve in the evapotranspiration and/or crop evapotranspiration, in particular in summer months (Figure 8.3 and Figure 8.4). In addition, the continuous application of amendments to address the alkalinity of applied alkaline water would result in salt build-up and increase of osmotic pressure. To ignore the leaching would result in short-term increased production, but likely lead to a rapid decline as salts accumulate and osmotic potential increase. To that end, it may be that any economic gain is completely offset by amendment volumes required to address sufficient irrigation water for the required leaching fraction irrigation volume. Therefore, it is prudent that land managers consider the leaching issues during land amendment and ensure a sufficient amount of water is applied to leach of salts from the root zone and/ or alternative management strategies to improve the agricultural profitability.

8.4.4. Economic viability of land amendment for agriculture

The results of the cotton yield clearly demonstrated that the spatial variability of yield was largely driven by the low irrigation distribution uniformity for both experimental sites. Despite this, yield improvement due to amelioration was observed, which highlights that land amendment has merit. On this basis, the economic assessment of land amendment for irrigated agriculture is largely confounded by system performance, but it was important to note that observations of increased productivity were made even in the face of inadequate amelioration of these sites; i.e. a basis for discussion given there is a complete paucity of this data at current.

There was a significant in increasing yield for application of sulphur-alone compared to lime and gypsum treatments. The application of sulphur appeared to have a major contribution to increase yield through the improvement of soil properties (Table 8.8). This effect was noticeable for both experimental sites where soil alkalinity and sodicity reduced (Figure 8.7 and Figure 8.8). For Site 1, the gypsum+lime+sulphur treatment provided greater yields resulting in the highest yield gain ($66/ha) but with a highest input cost, while sulphur-alone had lower gross income (higher than control), but lowest income. The sulphur-alone treatments resulted in the highest benefit, resulting in returning 49 and 3 AU$/ha gain for T3 and T4, respectively. The same trend was notable for Site 2, where the initial sulphur-alone resulted in the highest cotton yield and yield gain ($98/ha), followed by gypsum+sulphur treatment ($29/ha). For Site 2, the gypsum alone treatment showed $8.5/ha yield loss compared to control. Thus, the involvement of elemental sulphur appears to have a major role to increase the profitability for both sites.

Table 8.9 The treatment costs and yield gain of cotton yield for Site 1 and Site 2. The current cotton value is AU$500 per bale (Bartimote et al., 2017; Bennett et al., 2017). The amendment costs were 70, 80 and 666 AU$ for gypsum, lime and Sulphur for both sites, respectively. N.B. the cost: benefit of Site 1 was calculated based on the initial amendment cost as the cotton yield harvested in March 2018 while the reapplication of amendments occurred in April 2018; N.B. The cost benefit ratios should only be used to compare the treatments relatively, as the true cost benefit of the amelioration strategies is confounded.

Treatment		*Elemental Sulphur (kg ha^{-1})*	*Lime (kg ha^{-1})*	*Gypsum (kg ha^{-1})*	*Cost (AU$/ha)*	*Yield gain (AU$/ha)*	*Cost:Benefit ratio (AU$/ha)*
Initial	*Reapplication*						
				Site 1			
Control	Control	0	0	0	0	-----	-----
G_4L_2	G_4	0	2000	8000	720	65.5	11.0
$G_4L_2S_{100}$	G_4S_{160}	360	2000	8000	893	66	13.5
S_{200}	S_{160}	360	0	0	240	49	4.9
S_{100}	G_4	100	0	4000	413	3	137.7
				Site 2			
Control	$G_{2(2017)}$ $G_{2.3}S_{150(2018)}$	150	0	4300	401	-----	-----
G_2	$G_{2(2017)}$ $G_{2.3}S_{150(2018)}$	0	0	6300	541	-8.5	63.6
G_2S_{220}	$G_{2(2017)}$ $G_{2.3}S_{150(2018)}$	370	0	6300	687	29	23.7
S_{220}	$G_{2(2017)}$ $G_{2.3}S_{150(2018)}$	370	0	4300	547	98.5	5.6

Although, the effects of the initial amount of applied treatments to Site 2 were confounded on the yield due to the reapplication of amendments during the experimental period (2016–2018) which caused to a limitation in the decision making for the effects of amendments on improving yield. The highest yield was observed for initially sulphur applied plots. The profits of gypsum and lime amendments were less noticeable for both sites, this is speculated to be due to increasing osmotic pressure that limits the plant growth. However, the additional application of amendments had compromised the results and increased the uncertainty of the effect of amendments on the increasing yield as well as soil properties. This effect was not evident for Site 1 experimental plots because the provided cotton yield data was collected prior to reapplication of amendments in 2018.

Statistical analysis for Site 1 indicates even low application rate of sulphur (as low as 100 kg ha^{-1}) was efficient to increase the yield of cotton and was significantly different than control (no treatment) (Table 8.8). Although, the input cost was higher than the value of increased yield for the presented single cropping season, the total of increased yield of several crop season might pay off the input cost. In addition, the cost of land rehabilitation degraded by such marginal water and production lost might be much higher than initial amendment input (Bennett et al., 2019b; Orton et al., 2018). Therefore, appropriate management strategies with long lasting effects are necessary in order to preserve soil resource and agricultural productivity.

8.4.5. Using threshold electrolyte concentration to plan for strategic irrigation

The threshold electrolyte concentration (C_{TH}) is usually used to determine the suitability of marginal quality water to be applied to a soil. The C_{TH} has clearly been established as a soil specific (Bennett et al., 2019a; Bennett & Raine, 2012b; Dang et al., 2018d; McNeal & Coleman, 1966), and it is considered as a planning tool in terms of protecting hydraulic conductivity of soils. The results of C_{TH} demonstrate that the legacy of alkaline irrigation water may have affected the soil C_{TH} such that the current C_{TH} results are a function of equilibrium with the historic applied irrigation water quality. This is a rather likely scenario given the findings of Dang et al. (2018d) who demonstrated that field soils with historic irrigation using various levels of marginal quality irrigation water had undergone hydraulic reduction as compared to paired natural soils without any irrigation legacy. Consequently, the C_{TH} curves in this study show that the Site 1 soil appears to have undergone significant equilibration with the applied irrigation water quality and K_s reduction such that further irrigation does not cause further K_s reduction. This result is consistent with the paired natural and irrigated validation of C_{TH} in Dang et al. (2018d), however, the subsequent free alkalinity build-up issue is expected to cause potential soil structural degradation which cannot be observed from the C_{TH} curves. In comparison, Site 2 has the potential to undergo significant hydraulic conductivity reduction without appropriate management. It is likely that this site has not yet equilibrated with irrigation water quality, which is potentially only undertaking supplementary irrigation, rather than intensive irrigation. From this point of view, Site 2 has much to gain from not reducing hydraulic conductivity further in terms of potential yield penalties, and Site 1 should consider ameliorative strategies that take into account the current soil free alkalinity and constraints, as well as the irrigation applied to the receiving environment.

It is prudent to note for Site 1 that although there was no further K_s reduction predicted, there was differences in yield with treatments. This suggest that for this particular soil with small changes in pore geometry we get yield return. This further supports the environment already being degraded due to legacy of conditions. Therefore, land amendment with gypsum and sulphur would be expected to restore the land to some extent. For example, the SAR_{FC} and EC_{FC} of treatment 1 for the last sampling (i.e., after ~30 months) indicate that it will be expected that the soil K_s has improved from 8 to 1.5% reduction for Site 1 and from 58 to 5% K_s reduction for Site 2 in comparison to control plots for applied irrigation water of both sites. Based on the C_{TH} curves, the additional application of amendments that soils were subjected to, a greater improvement of soil structure would be expected, and this magnitude was significantly higher for gypsum treatments compared to control. This supports that fact that appropriate management is lowering SAR and maintaining the EC of soil solution, which is postulated to improve soil structure, infiltration and aeration (Bauder & Brock, 2001; Bennett et al., 2015a; Vance et al., 2008). However, such strategic management can be optimised through understanding of system dynamics in respect to soil-water interaction via considering rainfall patterns and subsequent water application to cause unforeseen rapid dilution events (Ali et al., 2018; Bennett et al., 2016b). In addition, gypsum can increase electrolyte concentration of soil solution in the short term, while the leaching or rapid dilution caused by rainfall may create stability concerns in the longer term (Ali et al., 2018; Shaw & Thorburn, 1985). The rapid dilution of the soil EC levels may drop below the critical flocculation level (i.e., C_{TH}), resulting in soil structural instability, and the reversible process associated with aggregation is not expected to occur spontaneously (Keren & Shainberg, 1981; Shainberg et al., 1981; Suarez et al., 2006). Given the fact that C_{TH} is soil-specific even within the same order (Bennett et al., 2019a), the mechanisms of each soil amendment and their synergistic effect to maintain soil structural stability would be specific. Therefore, an understanding of soil-water interactions and inherent soil structural response is necessary in determining the strategic use of marginal water for irrigation.

8.5. Conclusion

This study demonstrated that soil amendments have the capability to efficiently neutralise the alkalinity of groundwater under field conditions in New South Wales, Australia. A synergistic effect of amendments applied in combination was effective to chemically ameliorate applied alkaline and sodic groundwater and maintained soil properties of treated soils to the extent that could be expected given the magnitude of ameliorant application versus that of the total irrigation volume. Additionally, the HP1 model was not efficient predicting the changes in pH and HCO_3^-, of the receiving environment subject to irrigation and land amendment, which was postulated to be largely due to a series of complex soil-environment process that are not currently reflected in the solution based model. The resulting EC and SAR under land amendment and alkaline irrigation water application were more reasonably predicted, but improvement would be required. The outcomes of this study detailed caveats for the use of this model in land management strategy formulation, advising that the model can be useful in planning where adequate domain knowledge is involved in the planning process. Further investigation of land amelioration for alkaline irrigation water in the laboratory and field will be required to improve modelling outcomes for strategic planning.

8.6. References

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9. General discussion, conclusion and future research directions

9.1. General discussion

In the present study, the principal effects of irrigation water pH and alkalinity on the soil aggregate system and hydraulic conductivity dynamics have been investigated. The adverse effects of alkalinity on soil structural stability were also reviewed in the current models for water and solute movements in the soil. The factors affecting the soil specific response to soil structural stability have been identified to limit the deleterious effects of alkalinity. In addition, the efficacy of acidifying materials to neutralise the alkalinity of irrigation water at the broad field scale was assessed. The body of work conducted in this study showed several impediments to the current strategic use of alkaline irrigation water regarding the soil-specific response, especially for the use of the hydraulic conductivity reduction function in the HYDRUS model when planning irrigation water effects for a given soil.

This chapter provides a general discussion and framework of the effects of alkalinity and pH on soil structural stability, as well as the hydraulic conductivity dynamics in the HYDRUS model, and the limitations of this model, to predict soil physical and chemical properties subject to marginal irrigation water quality. The suggestions for the inclusion of guidelines/regulations are discussed to provide practical strategies in order to minimise soil resource and environmental harm. Finally, the considerations and management approaches for the use of current techniques are discussed in the context of marginal quality waters.

9.1.1. Improved soil hydraulic reduction dynamics within the HYDRUS model

The work of this thesis has clearly identified a limitation in the prediction of hydraulic conductivity reduction dynamics due to the pH of irrigation water in the HYDRUS model that clearly limits its accuracy. The soil response to the pH of irrigation water varied depending on the soil characteristics, such as original pH, clay content, clay mineralogy of soils as well as the ionic strength and pH of the irrigation water. This indicates that hydraulic conductivity reduction due to pH (K-pH-dependent model) should not be a generalised (linear) function. This study showed that the current K-pH-dependent function vaguely accounts for the scaling factor for K_s reduction and has substantial uncertainty regarding the hydraulic reduction properties of Australian and Californian soils. This study also clearly showed the limitation of the HYDRUS-1D model to predict K_s reduction (R^2=0.51) for the effects of pH (6–9) on K_s reduction of nine Australian soils, as well as unsaturated hydraulic conductivity for a subset of these Australian soils; the subset being subjected to 0, 100, 310 and 650 mg L^{-1} of HCO_3^- (R^2=0.54) for unsaturated hydraulic conductivity assessment using the major ion concentration module in the HYDRUS-1D. While the improved linear function provided superior performance in saturated and unsaturated conditions, as compared to the original HYDRUS linear function, soil-specific factors suggest that a nonlinear approach is more suitable, again for both saturated and unsaturated conditions.

The nonlinear model developed in this study provides a new specific form of hydraulic reduction function for the soil-water dynamic caused by the pH of irrigation water. This new model can then be used to substitute the current K-pH-dependent function in HYDRUS to determine the magnitude of K_s reduction at different levels of salinity and sodicity for a given soil. The HYDRUS software package implements a Marquardt-Levenberg type parameter estimation technique for inverse estimation of soil water, solute and/or heat transport parameters from measured steady-state or transient flow data (Šimunek et al., 2012), which the current nonlinear model is based upon. While the nonlinear model has much higher certainty for K_s reduction, having been successfully evaluated and calibrated at various levels of salinity and sodicity for the nine local and three Californian soils, it still treats the scaling factor approach for pH as independent to the scaling factor for soil SAR and EC built into HYDRUS. Clearly, there remains a need to enhance the nonlinear function to incorporate a more complete range of data in terms of SAR and EC in order for the nonlinear function to replace the entire scaling factor function within HYDRUS.

It has been established by Ezlit (2009) that the scaling factor used in HYDRUS for SAR and EC lacks the specificity required to adequately determine the threshold electrolyte concentration for soils. On this basis, the semi-empirical disaggregation model was developed (Ezlit et al., 2013), which improved upon the McNeal (1968) clay swelling model. Subsequently, an interim measure to include SAR, EC and HCO_3^- into the HYDRUS model via observed data is the inclusion of alkalinity (HCO_3^-) into the semi-empirical model of Ezlit et al. (2013) for determination of the C_{TH}.

However, the introduction of alkalinity into the disaggregation model increases the experimental treatments by another factor, meaning the approach quickly becomes logistically cumbersome and expensive in terms of time. For this reason, there was merit in seeking to use an adjusted SAR, whereby the effect of the alkalinity on Ca precipitation is corrected. This is a significant improvement in approach for prediction of broader disaggregation dynamics, but is of course more laborious than outright prediction due to the requirement to collect data. Just as Bennett et al. (2019a) found for SAR and EC with respect to C_{TH}, soil response is soil-specific for a given level of alkalinity as supported by the results for inclusion of alkalinity explicitly demonstrated for a soil's response to an irrigation solution and the soils ability to maintain aggregation — that is within the disaggregation phase and not breaching the aggregation-dispersion threshold (Dang et al., 2018a). The results of this thesis indicate that K_s use of an adjusted SAR for the inclusion of alkalinity effects is valid for reduction <30%. Beyond 30% hydraulic reduction there was a significant deviation between the predicted reduction using an adjusted SAR and the observed reduction for a system containing free alkalinity. On this basis, it is not warranted to include adjusted SAR as a generalised replacement for hydraulic reduction functions, indicating that non-linear approaches must be further improved. However, the prediction of the C_{TH} defined as a 20% reduction in hydraulic conductivity (Bennett et al., 2019a; Ezlit et al., 2013) can benefit. Therefore, it would be advantageous to develop a C_{TH} module for HYDRUS using an adjusted SAR. This would be a significant improvement.

The HYDRUS model is utilised globally for soil-water relations and to plan for application of irrigation waters to land. Therefore, it is prudent to ensure that appropriate caveats are applied to the current hydraulic reduction functions; i.e. they are not necessarily correct and indicative only, with a further requirement for observation data to be utilised in order to capture soil-specific responses in planning. The inclusion of the developed pedotransfer functions, and the use of an adjusted SAR for C_{TH} prediction must similarly carry caveats, as the data set of soils utilised is not substantial, even though it is likely the largest current global data-set. In improving the HYDRUS reduction functions, this work has highlighted that greater practitioner caution and understanding will be required. HYDRUS is a fantastic tool to facilitate planning, but there are tolerances relating to the safety of environmental function that is implicitly accepted when utilising it. The hope here is that this can be improved to educate the user such that these are explicitly understood, and uncertainty can be directly built into planning documents. There is certainly merit in improving the non-linear approaches, and this should remain a future focus as detailed above.

9.1.2. Alkaline irrigation water application guidelines in Australia

Globally, there are different guidelines for irrigation water quality parameters to ensure that irrigation water does not harm the soil resource and the environment. In Australia, the guidelines and recommendations are nationally agreed for managing water quality under the National Water Quality Management Strategy (NWQMS). The current guidelines in Australia and New Zealand are used as a guide to the appropriate selection of saline and sodic water to maintain soil hydraulic conductivity (ANZECC, 2000). The ANZECC (2000) guidelines do not specify alkalinity and pH effects on the soil structure stability and hydraulic conductivity. Instead, it is described that the prolonged use of alkaline irrigation water can lead to an excess of bicarbonates in the soil system, and there is an increased affinity for Ca^{2+} and Mg^{2+} to precipitate as insoluble carbonates in the soil. The reduction in Ca^{2+} and Mg^{2+} is described to result in an increased SAR, which may negatively impact on soil structure. However, no trigger values for bicarbonate and pH are recommended in irrigation water guidelines within Australia and New Zealand. The exception being that it is generally reported that bicarbonate greater than 100 mg L^{-1} can cause issues for irrigation equipment (i.e. filters and drippers) and plant growth (ANZECC, 2000; DAF, 2014). The work in this thesis clearly demonstrates that irrigation guidelines for use of alkaline water are a global imperative.

The appropriate inclusion of an alkalinity guideline for soil security (Bennett et al., 2019b) is paramount to the future of national irrigation schemes in Australia, and globally. However, the effect of alkalinity/pH on soil structural stability varies depending on the soil properties and the chemical composition of applied irrigation waters. Hence, a generalised criteria for the use of irrigation water alkalinity, sodicity and salinity in the formulation of guidelines would not be appropriate, unless such general guidelines serve the majority of the soils. Bennett et al. (2019a) discuss the same point for the C_{TH} of soils in relation to the ANZECC guidelines, concluding that generic guidelines should be altered to ensure that the vast majority of soils would not be impacted by incorrect advice from a generic guideline. This could be thought of as two standard deviations, for example, which would result in very conservative guidelines. However, the guideline should then specifically state how a variation to the generic guideline could be obtained, specifically pointing towards which test might need to be undertaken. Similarly, alkalinity must be considered within the matrix of soil structural effects due to irrigation water quality. However, the question remains as to what constitutes a generic guideline such that it is an acceptably conservative measure.

The effects of alkalinity on reduction in K_s are well established to be result of an increase in the relative sodium concentration in the soil exchange-solution system, as Ca^{2+} and Mg^{2+} precipitate (Chorom, 1996; Suarez et al., 1984), organic matter dissolves (Lieffering & McLay, 1996) and clay minerals disassociate (Amram & Ganor, 2005). The body of work in this thesis clearly demonstrated that the effects of alkalinity/pH are dependent on the clay content, mineralogy, initial soil pH, SAR, and ionic concentration of the solution under saturated and unsaturated conditions. Each of these factors can change the extent of adverse effects of alkalinity in causing soil structural degradation and then reducing soil K_s. In addition, a greater extent of soil structural degradation and K_s reduction might occur where marginal irrigation water quality is not well managed, or a soil receiving it is unable to withstand it. However, there remains limited information on the issues associated with alkalinity regarding the acceptable minimum level and reduction in K_s of Australian soils. It is clear that the establishment of alkalinity threshold (Alk_{TH}) level is crucial to determine practical values for the decline in soil pore geometry and K_s reduction, which varies depending on soil types. The Alk_{TH} should assure the maintenance of soil structure and hydraulic dynamics for individual soils, which could be suggested as 100 mg L^{-1} based on the discussion in the ANZECC (2000) guidelines. However, the work in this thesis has highlighted that using 100 mg L^{-1} as a generic threshold is not suitable for all of the investigated soils. Given the fact that soils have heterogeneous properties and soil-specific response to the marginal quality waters (Bennett et al., 2019a; Dang et al., 2018d; Shainberg & Letey, 1984), the development of a generic Alk_{TH} might not be a practical strategy.

The literature indicates that the residual alkalinity in irrigation water varies depending on the electrolyte concentration and the concentration of divalent cations (i.e. Ca^{2+} and Mg^{2+}) (Eaton, 1950; Van Beek & Van Breemen, 1973). Where the concentration of divalent cations increases the HCO_3^- precipitates, resulting in lower residual alkalinity in the solution. Bennett and Raine (2012a) also discuss that the electrolyte concentration is a crucial factor to change the level of residual alkalinity in the irrigation water (Figure 9.1). Figure 9.1 suggests that depending on the electrolyte concentration the concentration of HCO_3^- greater than 100 mg L^{-1} water may be considered as a source for irrigation without causing soil degradation, although this is only for SAR=15 as an example, and is expected to vary with SAR as well. Additionally, while Landon (1984) has established a generic maximum limit for residual alkalinity to be 2.5 $mmol_c$ L^{-1} for irrigation water, DAF (2010) and Rengasamy et al. (2010) discussed that the effect of alkalinity concentration greater than 1.25 $mmol_c$ L^{-1} can be expected to cause structural degradation problems for soils. The results in this thesis support the use of the lower residual alkalinity value. Further consideration of residual alkalinity and the effects on structural degradation for a broader range of soils would be worthy of consideration in establishing a guideline threshold.

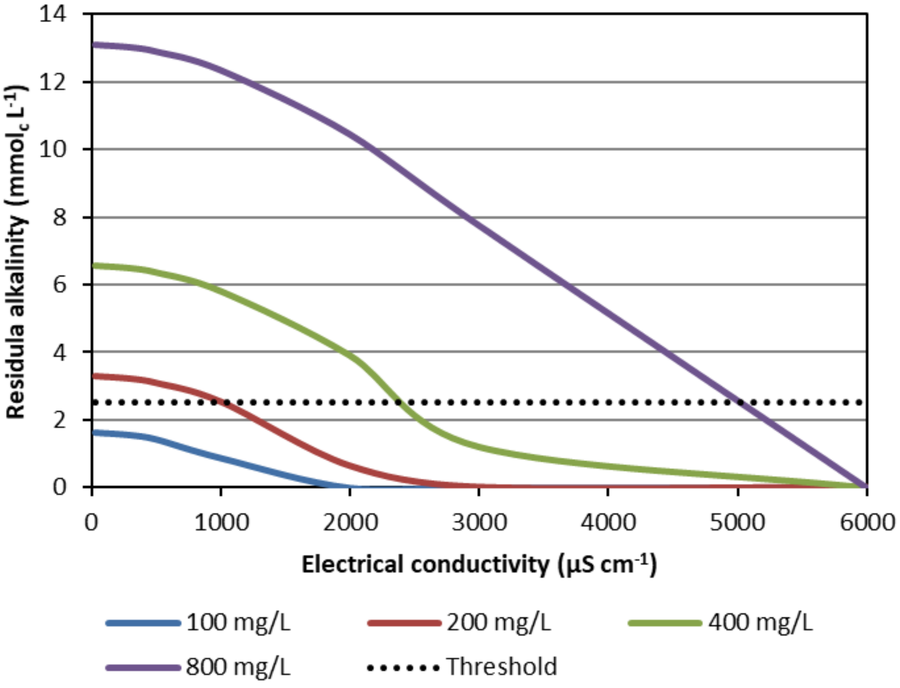

Figure 9.1 Expected residual alkalinity resulting from different bicarbonate solution concentrations at SAR 15 with the change in EC (Bennett & Raine, 2012a). The threshold value is residual alkalinity 2.5 $mmol_c$ L^{-1} as defined by Landon (1984) as the upper limit of marginally suitable irrigation waters. Calculations are consistent with Rayment and Higginson (1992).

Given the ANZECC (2000) guidelines are nationally utilised in decision-making for environment protection in Australia, land use management, natural resource management and agricultural irrigation water management, the inclusion of a residual alkalinity value for consideration of water quality safety is prudent. Furthermore, it remains important to reduce the significant uncertainties associated with the derivation and application of water quality guidelines within the ANZECC (2000). Therefore, it is proposed that a residual alkalinity guideline of 1.25 $\mathrm{mmol_c\ L^{-1}}$ could be used as a conservative measure on the basis of the literature and the results obtained in this thesis research. This should serve the vast majority of soils, but can be upgraded, or downgraded, in the future by considering the factors contributing to the soil structure stability for a much broader range of soils than the nine selected in this thesis. In the interim, a conservative threshold would appropriately protect the soil resources and minimise harm to the environment.

9.1.3. Towards a practical implementation framework for alkaline irrigation

Consideration of why the CSG industry regulations for marginal quality water regulations have been put in place is highly pertinent in the discussion of a framework for the practical implementation of marginal quality irrigation water within agriculture. As has been identified in the above sections there are numerous environmental concerns associated with the application of marginal quality irrigation water to land. As climate pressures increase the industrial demand for freshwater and overland flow water resources, the importance placed on these environmental concerns must progressively increase because marginal quality water will become a strategic resource. Within the Australian coal seam gas (CSG) industry, the import placed on environmental resource protection is such that the poor, to marginal, quality water extracted with the CSG is considered a waste, and application to land as disposal. Use of these terms is deliberate in that it suggests the water must be treated, or managed very specifically for a particular receiving environment, to be considered a resource. The CSG industry also requires approval for application of the water to land, due to the potential for land degradation. In fact, where approvals are provided, this is effectively a licence—containing strict scope and conditions—to cause a controlled level of degradation to the receiving environment for such water. Hence, the language of ‘waste’ and ‘disposal’ also helps to reinforce this. At this juncture, it is useful to consider that the quality of extracted water from the Queensland CSG industry (Bennett & Raine, 2012a; Kinnon et al., 2010) is similar to the groundwater quality used for irrigation, without regulatory restriction, in the Condamine and St George agricultural irrigation regions (Biggs, 2011; Biggs et al., 2013; Melland, 2016). Considering this, it is proposed that an approach similar to that used in the CSG industry for identifying groundwater as a waste or resource may be useful in terms of maintaining soil security (Bennett et al. 2019b) within our agricultural regions.

The Queensland State Government has mandated that coal seam (CS) water be utilised under an approval system where there exists both a general and beneficial use approach to gaining approval (Department of Environment and Heritage Protection, 2014). The general use approval (GUA) has clear standards and does not need individual assessment of the receiving environment, while the beneficial use approval (BUA) requires individual assessments of both the potential irrigation water quality and the soil condition of the receiving environment, including its capability to receive the water in natural and/or treated form. The GUA is usually a highly conservative set of thresholds for the characteristics of the water in question that has the intention of causing minimal environmental harm for the majority of receiving environments. The GUA does not guarantee that no land degradation will occur, instead, it limits the risk to as low as reasonably possible. On the other hand, water qualities considered under the BUA may be suitable for use in some receiving environments, but cause degradation in others. Hence, beneficial use is water quality and receiving environment specific. If used correctly, beneficial use of such waters can be encouraged in a way that maximises production as well as protects the soil resources and the ecosystem. Therefore, the following sections work towards defining an approach for general and beneficial use of marginal quality saline, sodic and/or alkaline irrigation water, based upon the work in this dissertation research and the literature.

9.1.4. Establishment of a general use approval

The provision of a general use approval (GUA) for the application of alkaline and sodic water could significantly assist land managers by making clear where further consideration of the water quality suitability to the receiving environment is not needed. This is the current situation for all waters, but most certainly should not be so given the weight of information for land degradation in the presence of sufficient sodicity, salinity and or alkalinity (Fitzpatrick, 2002; Oster, 1994; Qureshi et al., 2011; Rengasamy et al., 2010). The determination of the C_{TH} is currently costly and laborious (Dang et al., 2018b), and even though the analytical process could be largely automated the cost would remain in the order of \$500 to \$1000 in terms of operator time and report preparation. The aim of the GUA is to ensure marginal quality waters limit the risk of soil resource deterioration, yield reduction and environmental harm. The guidelines and requirements should therefore infer considerable restriction and minimum standards for the use of marginal quality waters that could be utilised in a manner accepted to provide a definite benefit to the land managers and the environment.

In terms of soil structural relations, the GUA for irrigation with extracted groundwater must consider the following water quality characteristics:

1. Monovalent to polyvalent cation concentration in solution;
2. The salinity of the water; and,
3. The alkalinity of the water.

Literature has well established the relationship between EC and SAR in terms of soil structural stability, from the seminal work of Quirk and Schofield (1955) through to more recent work of Bennett et al. (2019a). The major learning from this work is that the response of soils to soil structural degradation, given a particular water quality, is highly soil-specific (Bennett et al., 2019a; Dang et al., 2018a; Dang et al., 2018d; Zhu et al., 2019b). Therefore, the establishment of a GUA for salinity and sodicity needs to consider the range of measured response in the C_{TH} and develop a general threshold based on minimum impact to soil structural stability. This must weigh the salinity and sodicity GUA in favour of the environment. To investigate this, it is worth considering both the 90 and 95th percentile of observed C_{TH} for the 58 soils in Bennett et al. (2019a) and 4 soils in Ali et al. (submitted) [Chapter 7]. The establishment of 95% percentile as the soil C_{TH} GUA upper boundary can be expected to significantly support the environment compared to classical definitions of C_{TH} boundary guidelines provided in the ANZECC (2000) document (Figure 9.2a). The use of two standard deviations was explored (effectively the 97th percentile) and resulted in a GUA boundary at 8.0 dS m^{-1} of SAR=3, although this is perhaps too conservative. Use of the 90th percentile did not increase the potential GUA boundary all that much from the 95th percentile, which could suggest it as applicable, or that the dataset contains outliers. However, the dataset is too small to reliably account for outliers.

It is suggested that the 95th percentile is reasonable at this point, but that further work must be done to expand the variety of soils used to define the boundary. Assuming we accept the use of the 95th percentile as the GUA boundary, the suitability of irrigation water in terms of salinity, sodicity and alkalinity (calculated as adjusted SAR) can be assessed based on the proposed new guideline using Figure 9.2b. In terms of comparing this to the current ANZECC (2000) guideline, it is clear that the 95th percentile approach is more conservative, but also serves to highlight that agriculture has been potentially utilising irrigation water that has a much greater likelihood to cause environmental harm than might be considered reasonable since the ANZECC (2000) guideline was introduced.

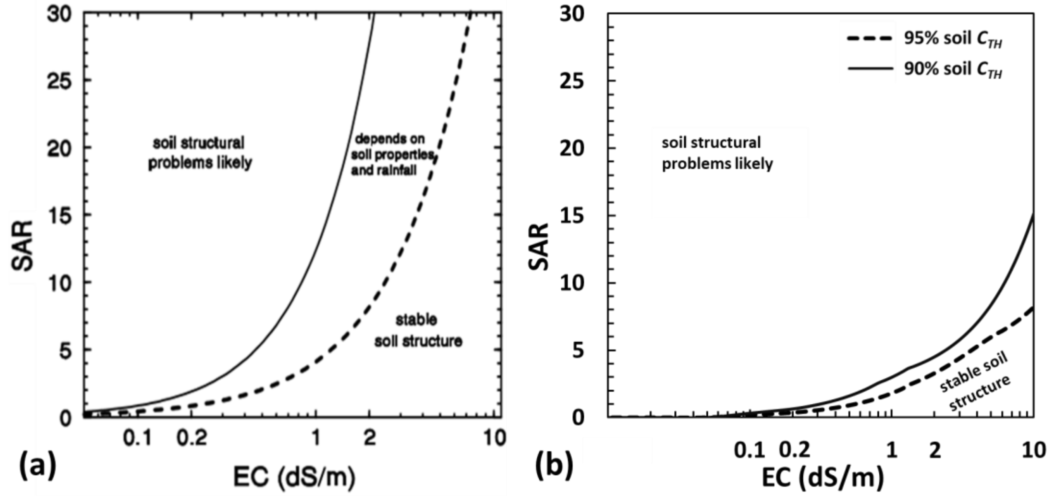

Figure 9.2 Comparison of the relationship between electrical conductivity (EC) and sodium adsorption ratio (SAR) for soil structural stability (C_{TH}) as it appears in ANZECC (2000) and (b) 95 percentile of C_{TH} (20% K_s reduction) for 58 soils in Bennett et al. (2019a) and 4 soils in Ali et al. (submitted). Figure (b) includes the C_{TH} of 31 Vertosols, 14 Chromosols, 10 Dermosols, 2 Kandosols, a Kurosol, a Sodosol and a Tenosol. The dashed and solid black lines are 95 and 90% confidence of soil C_{TH}, respectively.

While the effect of irrigation water alkalinity on soil structural stability is mainly dependent on the ionic composition and SAR of the water, where alkalinity can largely be accounted for via adjustment of the SAR to some extent (see Chapter 7), alkalinity can also have a greater effect depending on the residual alkalinity magnitude. Residual alkalinity is also a function of the ionic concentration and the SAR. Therefore, as has been discussed in the above sections, the residual alkalinity must be used to assess the suitability of water sources for irrigation purposes. DAF (2010) and Rengasamy et al. (2010) have identified a threshold level of residual alkalinity as low as 1.25 $\text{mmol}_c\ \text{L}^{-1}$ for Australian soils, with 2.5 $\text{mmol}_c\ \text{L}^{-1}$ used more widely (Landon, 1984). These threshold levels of residual alkalinity are somewhat arbitrary values, constructed as a safety guideline based on observational research for a range of likely environmental conditions. For this reason, they might not serve the soil resource and the environment, due to soil specific response to the marginal quality irrigation water. Therefore, the GUA needs to set a threshold that is likely to serve the full range of probable to encountered conditions. Within this dissertation, it was observed that for some soils deterioration in structure occurred when residual alkalinity greater than 1.25 mmol$_c$ L^{-1} was encountered. Based on this observation, it is suggested that the GUA should utilise the more conservative residual alkalinity value prescribed by DAF (2010) and Rengasamy et al. (2010).

In investigating this further, Figure 9.3 was produced to demonstrate the 1.25 mmol$_c$ L^{-1} threshold against a reasonable range of likely irrigation water qualities (EC of 0–80 mmol$_c$ L^{-1}, SAR of 0–100, and alkalinity of 50–1000 mg L^{-1}).

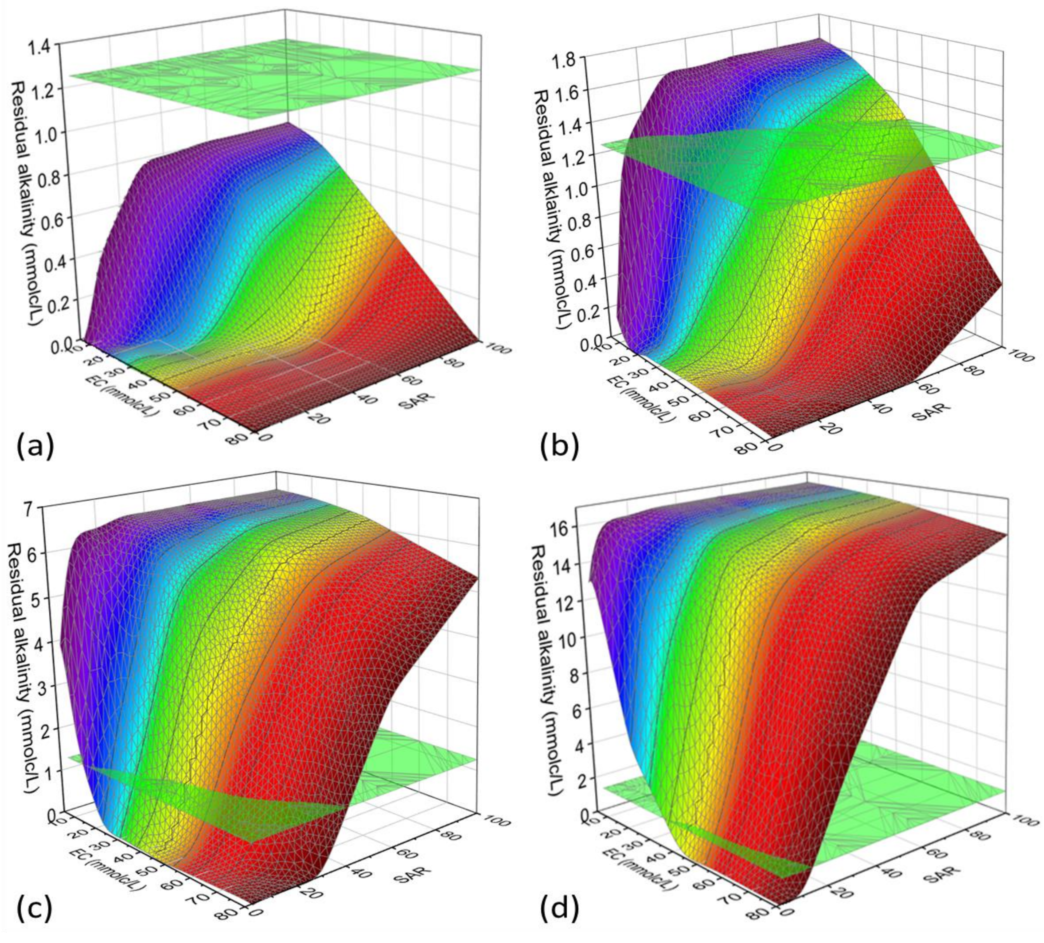

Figure 9.3 The expected residual alkalinity at different level of electrolyte concentration and sodium adsorption ratio (SAR; (mmol$_c$ L^{-1})$^{0.5}$) calculated for alkalinity (HCO_3^-) of a) 50, b) 100, c) 400 and d) 1000 mg L^{-1}. The light green plane represents the threshold residual alkalinity (1.25 mmol$_c$ L^{-1}) (DAF, 2010; Rengasamy et al., 2010). The residual alkalinity calculation is consistent with Rayment and Higginson (1992).

The analytical modelling indicates that as the solution alkalinity approached 100 mg L^{-1} from 50 mg L^{-1} the residual alkalinity threshold of 1.25 mmol$_c$ L^{-1} was breached, irrespective of solution concentration or SAR. This suggests that an absolute alkalinity concentration as a GUA characteristic would be <70 mg L^{-1}.

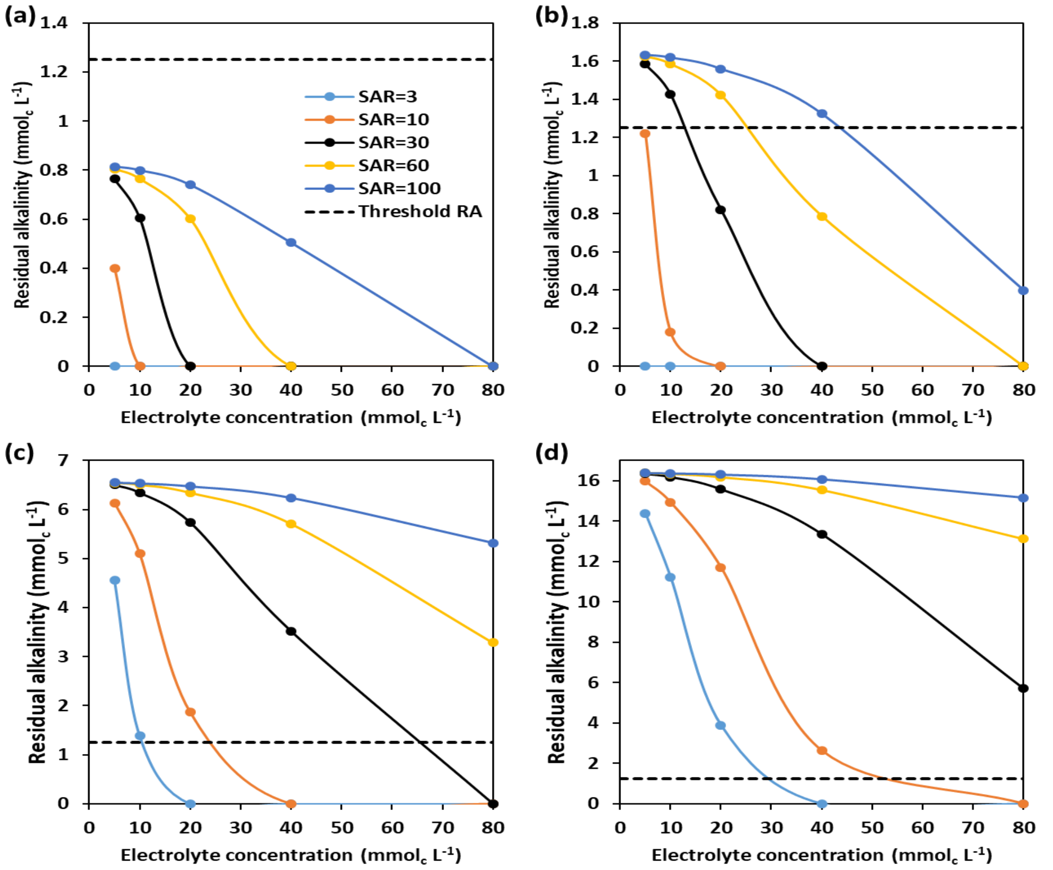

Figure 9.4 The expected residual alkalinity, from the perspective of alkalinity and electrolyte concentration, at different levels, of electrolyte concentration and sodium adsorption ratio (SAR; (mmol$_c$ L^{-1})$^{0.5}$) calculated for alkalinity (HCO_3^-) of a) 50, b) 100, c) 400 and d) 1000 mg L^{-1}. The dashed line represents the threshold residual alkalinity (1.25 mmol$_c$ L^{-1}) (DAF, 2010; Rengasamy et al., 2010). The residual alkalinity calculation is consistent with Rayment and Higginson (1992).

Looking more closely at the residual alkalinity from the perspective of solution concentration (Figure 9.4) that the suitability of alkaline irrigation water can be increased via increasing the electrolyte concentration of irrigation water for the same SAR and alkalinity content. However, the increase in salinity can also have a potential negative effect on plant growth when exceeding the salt tolerance level of plants. Therefore, the selection of irrigation water quality should not only be based on the soil structural stability but also a specific salt tolerance of plants with consideration of leaching factions and deep drainage issues in irrigated lands.

Considering the discussion above, a proposed GUA is detailed in Table 9.1.

Table 9.1 The proposed general use approval (GUA) for electrolyte concentration, sodium adsorption ratio, alkalinity (HCO_3^-) and residual alkalinity of irrigation water application.

Water characteristic	*Unit*	*Critical values*					
Electrolyte concentration*	dS m^{-1}	<0.2	0.5	1.0	2.0	4.0	8.0
Sodium adsorption ratio	$(\text{mmol}_c\ L^{-1})^{0.5}$	0.36	1.1	2.0	3.3	5.3	7.4
Alkalinity	mg L^{-1}	<70					
Residual Alkalinity	$\text{mmol}_c\ L^{-1}$	<1.25					

* Electrolyte threshold determined by crop salinity threshold and leaching fraction requirement (Shaw & Thorburn, 1985).

9.1.5. Considerations of beneficial use approval for alkaline irrigation water

The beneficial use approval (BUA) usually involves precise and strategic management of lands through specific assessment of available water quality, soil condition and the regime of irrigation water application. The major irrigation water assessment is the determination of total dissolved ions, SAR, alkalinity and the pH that are responsible for soil structural degradation. Given that variation in these factors causes soil aggregate swelling, disaggregation, and clay particle dispersion, with concomitant degradation of soil structure and hydraulic conductivity (Ali et al., 2019a; Chorom et al., 1994; Rengasamy & Marchuk, 2011; Shainberg et al., 1981), the assessment of the interrelation of EC, SAR and alkalinity to cause soil structural degradation must crucially be based upon the soil specific response. The results obtained in this thesis research clearly indicate that any increase of alkalinity (as low as 100 mg L^{-1}) in irrigation water will result in the K_s reduction of soils at different extents based on their properties, and ionic compositions and SAR of applied irrigation water.

The C_{TH} of soils is an important index for assessing the degradative effects of marginal quality irrigation water on the soil structural stability. The incorporation of alkalinity into the current C_{TH} is a strategic approach to precisely manage irrigation water application because alkalinity is a major component in most available water sources within arid and semi-arid regions of Australia. The results presented herein confirmed that there is a strong relationship between the C_{TH} reduction of K_s produced by non-alkaline and alkaline solutions represented as SAR and adjusted SAR for up to 30% K_s reduction. This association indicates that the alkalinity (HCO_3^-) can be successfully incorporated into the current disaggregation model to determine C_{TH} (≤20% K_s reduction). In essence, the C_{TH} is used as it presents a safety factor for soil structural management. Menezes et al. (2014) discuss that the decision on the suitability of marginal quality water mainly depends on the initial absolute hydraulic conductivity of soils, and indicate that >80% K_s reduction in soils with high initial K_s could be well be accepted. Therefore, in negotiating a BUA, the absolute hydraulic conductivity may be a factor for consideration, although it is rarely collected within field environments. However, as the effect of alkalinity on the soil structural stability, hydraulic conductivity and land degradation varies based on the soil specific properties, there is a requirement to consider this in conjunction with the current C_{TH} approach rather than in isolation.

Overall, the soil properties (especially clay content and alkalinity) play important roles in the variation of soil K_s reduction restrictions under alkaline irrigation water application; the K_s reduction is increased with lowering clay content in soils. However, the mechanisms of soil structural degradation, and K_s reduction, for alkalinity and high pH differs to those of sodicity. This indicates that the management of lands with the contribution of alkalinity must be different compared to the occurrence of sodicity and salinity without an alkalinity constraint. The principal difference is due to alkalinity effects on organic matter dissolution, mineral dissolution and increasing the sodium proportion of the soil solution and exchange phase via calcium and magnesium precipitation. In addition, this thesis research clearly showed that the potential effects of alkalinity to induce soil structural degradation and hydraulic dynamic reduction and suggests that the major considerations for the strategic management of alkaline irrigation waters include

- Soil clay content and mineralogy
- Organic matter and oxides in soil
- Initial alkalinity condition of soils throughout the soil profile
- Initial permeability of soil
- Cation exchange capacity
- The exchangeable sodium percentage, dispersivity and salinity of soil

- Alkalinity, pH, sodium adsorption ratio and salinity of irrigation water

Mismanagement of alkaline irrigation water can increase the potential for soil structural degradation and crop production limitations in the long-term. Acid forming materials provide a potential solution for the strategic and beneficial utilisation of alkaline water sources, such as CSG water and other marginal artesian waters in Australia, whereby waters of poorer quality than the C_{TH} and Alk_{TH} metrics advice can be used in conjunction with treatment options. Elemental sulphur and/or sulphuric acid are effective amendments that can be utilised for neutralising the alkalinity of irrigation water. The acidifying amendments can be added directly to soil [Land amendment irrigation strategy; see Bennett et al. (2016b)] and/or applied to irrigation water prior to irrigation. The adequate amount of amendments for a solution can be calculated through using the PHREEQC geochemical model in planning the alkalinity amelioration. However, strategic amelioration planning requires precise management based on the site condition, the regime and amount of alkaline irrigation water application, efficiency of ameliorants, existing free alkalinity and soil buffering, as well as the climatic factors such as rainfall intensity, magnitude and frequency.

Irrigation regimes depend enormously on the season of growth and crop type. Crops planted at the start of the wet season are reliant only on supplementary (less than 50% irrigation required) irrigation to maintain available water in the root zone. In contrast, for drier seasons, or environments, agricultural production may be completely reliant on irrigation. Between these scenarios, there might be opportunistic use of an alkaline irrigation water source to top up available water and crop yield depending on the available water and rainfall, as well as commodity prices. Thus, BUA ameliorative management for alkalinity should consider the water application regimes to avoid over-acidifying soils and the accumulation of salts.

Increasing salinity is traditionally acknowledged to decrease the adverse effects of sodicity on soil structural stability. However, the extent of salinity within the irrigation water also must be considered from a crop production perspective. Additionally, depending on the irrigation regime, the use of irrigation water containing appreciable salts is likely to result in an accumulation of salts within the root zone, unless a leaching fraction is developed (Shaw & Thorburn, 1985). On the other hand, caveats are required to manage deep drainage risks in irrigated lands during irrigation with high salt waters and application of sources of salts to soil (Biggs et al., 2012). The salinity of leachates is typically high and usually much higher than underlying groundwater, unless they are already saline (Silburn et al., 2013), meaning that a leaching fraction must consider that deep drainage has the potential for recharge of shallow overlying water reserves of fresh quality. Hence, in order to avoid complicated issues within the soil, an appropriate strategic management is required to neutralise alkalinity without undue salinity build-up and/or assuring adequate leaching of salts without recharge of shallow freshwater reserves.

Additionally, appropriate amendment strategies should be applied to address the alkalinity of irrigation water, while considering the possibility of rapid dilution caused by rainfall. Rapid dilution during rainfall, or switching directly to a good quality irrigation water with low solution concentration in a land previously irrigated with alkaline and sodic water, could negate the amendment effect and deteriorate soil aggregation and soil hydraulic conductivity (Dang et al., 2018d; Sumner, 1993).

With respect to the above discussion, the research here suggest that a BUA must consider:

1. The water quality of the irrigation source, and potential for variation in it in terms of the following factors:
    a. Electrolyte concentration
    b. Sodium adsorption ratio
    c. Total alkalinity
    d. pH
    e. Total dissolved ions
2. The receiving environment soil capability to receive the water quality, with consideration of spatial variation in this on the basis field production variability and soil type variability:
    a. Threshold electrolyte concentration, including alkalinity adjustment, for each unique unit determined
    b. Water quality plotted against the alkalinity adjusted threshold electrolyte concentration and suitability determined
    c. If unsuitable, treatment may be considered

3. The treatment requirement of the water can be determined using geochemical modelling software such as PHREEQC and needs to be reported in terms of kilograms of amendment per mega-litre of irrigation per hectare (kg ML^{-1} ha^{-1}).
4. The irrigation regime in terms of the volume of water applied and subsequent effect on management:
   a. Reliant regime
   b. Supplementary regime (defined as occurring every season cropped with less than 50% of the reliant regime irrigation requirement)
   c. Opportunistic regime
5. The requirement for a leaching fraction based on the water quality, the treatment requirement, the irrigation regime, and the likelihood of expected regional rainfall. The leaching fraction must consider the potential for deep drainage, aiming to keep salts stored within the vadose zone below rooting depth and above freshwater reserves. The use of HP1 in HYDRUS could be useful in planning these regimes, but as demonstrated in Chapters 6 and 8 this does suffer from some issues in predicting pH and alkalinity dynamics. Irrespective of this, irrigation and drainage should be modelled to protect soil security and water reserves. This requires the following soil characteristic data determined for each unique spatial unit:
   a. Electrolyte concentration
   b. pH
   c. Existing alkalinity and buffering capacity
   d. Soluble and exchangeable cations
   e. Cation exchange capacity
   f. Particle size analysis
   g. Soil water characteristic curve

Where these considerations are taken into account, a prudent BUA could be issued that limits environmental harm on a soil-specific, spatial basis, while also increasing production potential in water limited and strategic irrigation environments.

9.2. General Conclusion

The main focus of this project was to investigate the effect of pH and alkalinity of irrigation water on the range of soils with different physical, chemical and mineralogical properties. The effect of pH on the soil clay dispersion and hydraulic conductivity for acidic, neutral and alkaline soils was investigated. This study was important in assessing the current function for the hydraulic reduction due to pH in the HYDRUS model, and improvement of the current mathematical function toward soil specific response to pH for the Australian soils. The ability of the HYDRUS model as a soil water movement simulation tool was further tested to simulate the potential changes in the soil physicochemical properties under an unsaturated condition. The comparison of the current and the developed functions were performed to evaluate the improvement of the prediction model. Furthermore, the incorporation of the alkalinity (HCO_3^-) into the current disaggregation model of Ezlit et al. (2013) to determine C_{TH} improve confidence in C_{TH} determination and prediction of soil degradation. Management strategies also were investigated, and the limitations of these approaches discussed in relation to the successful amelioration of alkaline irrigation water and the soil. The results of the experimental research presented in this thesis have provided a comprehensive understanding of the factors affecting the soil structure and their interactions toward soil specific structural stability under alkalinity. In relation to the topics and themes investigated in this study, the following conclusion can be drawn:

- The body of research clearly showed that when alkaline water is considered as a source of irrigation, thorough evaluation of water quality, soil type and initial soil physical, chemical and mineralogical properties is required in order to develop correct managements.
- The effect of irrigation water pH on soil structural degradation depends on the soil specific properties, particularly on soil clay content and mineralogy, as well as the ionic strength of the water.
- Specifically, the experimental results demonstrated that the effect of alkaline and high pH irrigation water was the lowest on smectitic, high clay content soils, but in contrast vastly different from the effect of the same irrigation water on the low clay content, acidic kaolinitic soils and illitic soils, which were highly affected, exhibiting soil structural deterioration, disaggregation, clay dispersion and reduction in K_s. This is a clear indication

that the strategic use of marginal quality irrigation water requires management practices that consider the soil-specific response.

- A review of the soil K_s reduction due to the pH of irrigation water, known as the r_2 scaling factor in the HYDRUS model clearly showed that this K_s reduction coefficient overestimates K_s reduction with increasing pH, which limits its accuracy. It has been confirmed that the response of soils for the increase of pH is soil-specific, suggesting that the r_2 scaling factor should not be a linear (generalised) function. Based on the results of K_s reduction for a range of Australian soils, generalised and nonlinear functions were formulated to replace the r_2 scaling factor in the HYDRUS model. These two new functions have been successfully calibrated and evaluated with the change in K_s due to variation of pH from 6 to 9 for both Australian soils used in this study and Californian soils examined by Suarez et al. (1984). The results showed that these functions performed objectively well to describe the change in K_s due to pH compared to the current r_2 scaling factor in the HYDRUS model, and further indicate that a nonlinear function provided a greater accuracy, due to soil specific K_s prediction in saturated and variably saturated conditions.
- For the evaluation of the HYDRUS-1D model to predict the soil chemical and physical properties of irrigated soils under unsaturated condition, the modelling results confirmed that the overall trends and key chemical reactions could be simulated. However, results show that the model over-estimates the effects of alkalinity (HCO_3^-), in particular, the soil pH and HCO_3^- and reduction in hydraulic conductivity. The prediction of K_s change by the current HYDRUS model was significantly from the observed K_s compared with two newly developed models (generalised and nonlinear models). This study confirmed that the HYDRUS model requires revision to accurately predict the changes in soil physicochemical properties.
- The limitation of the current C_{TH} model is that is based on the Na and Ca system, without considering the adverse effects of alkalinity (HCO_3^-) on the soil K_s reduction. The results indicated that any increase in HCO_3^- (as low as 100 mg L^{-1}) resulted in further reduction comparing to the normal C_{TH}. Incorporation of HCO_3^- into a semi-empirical disaggregation model was only valid up to 30% reduction in K_s accounting for Ca and Mg precipitation. This supports the hypothesis that the use of the disaggregation model with HCO_3^- can be accepted for C_{TH} (where ≤20% K_s reduction). The further K_s reduction due to HCO_3^- is

described to be beyond the increase of Na proportion through Ca and Mg precipitation. Therefore, the incorporation of HCO_3^- into disaggregation model could be a significant management practice where HCO_3^- presents in the irrigation water, in particular for the use of wastewaters and industrial by-product water such as CSG water in Australia and the USA.

- This research indicates that current Australian and New Zealand guidelines need to consider the effects of the alkalinity of irrigation water in regulations and guidelines to as well as specific properties of soils under irrigation with alkaline water. The other negative effects of alkalinity beyond increasing sodicity should also be considered.

With regard to the viability of gypsum and sulphur use as an alkalinity amendment, some conclusions are:

- The application of sources of sulphur is efficient to lower the soil pH and bicarbonates in particular for the long-term (year 2 and 3) and the re-application of these amendments in longer term.
- Soil amendments improved soil structure and hydraulic conductivity based on the predicted C_{TH} with using adjusted SAR and electrolyte concentration, this effect was higher when gypsum involved.
- The combination of lime with gypsum did not provide an appreciable soil improvement, but rather increased the alkalinity of soils for the short-term (6 months) especially in the soil surface. These effects were neutralised by re-application of sulphur and gypsum.
- Considering deleterious effects from alkaline irrigation water, it is recommended that acidifying amendments (i.e. gypsum and sulphur) be applied annually to neutralise the alkalinity. When irrigation water with low SAR applied on a non-sodic soil, the gypsum might not necessarily be required, while a sufficient amount of sulphur could neutralise the alkalinity.
- Application of sulphur resulted in some economic return and a reduction in potential yield loss through increasing the cotton yield.
- The HP1 module was not sufficiently able to predict the changes in soil solution chemistry for land amendment under alkaline irrigation water application in the field. This confirms

that these caveats of HP1 model are required to be presented for the land amendment strategies.

9.3. Recommendations for future work

As a result of the work reported in this thesis, various suggestions for future research have been identified and the following studies are recommended.

- Investigating the impact of varying pH of irrigation water on K_s reduction will be essential for a broader range of soils that have varying pH and varying clay content within each pH subclass. The clay content and soil pH proved to affect the degree of the K_s reduction. In this study, the effects of acidic initial soil pH interacted with lower clay content, while the nonlinear scaling factor function formulated in this study appeared to have offset in terms of the effect of clay content.
- Evaluation of the HYDRUS model under sequential alkaline irrigation water and rainfall events in the field and crop growth condition. This may improve the certainty of the applicability of this model to simulate the changes in soil due to alkaline irrigation water in the natural condition.
- Development of a pedotransfer function to predict the change in soil K_s due to salinity, sodicity and alkalinity to serve the soil specific (i.e. combination of r_1 and r_2 scaling factors). The incorporation of such function into the HYDRUS model and using the proposed pedotransfer function (nonlinear function) developed in this study for the pH effect on K_s reduction.
- Even though the prediction of the C_{TH} has been well examined and validated by soil scientists, there is still room for improvement through considering the net negative charge variation under different levels of alkalinity, which is identified to be a primary reason for the soil structural degradation and K_s reduction in this study. The relationship between K_s reduction and net negative charge (zeta potential) and the percentage of dispersed clay should be investigated and the factors affecting these can be explored. This is expected to help the C_{TH} determination more conveniently for explaining soil specificity through the consideration of soil properties to develop a pedotransfer function for soil specific response, as this thesis indicated the generalised function is not appropriate.

- Based on the findings of this study that alkalinity results in the K_s reduction beyond the Ca and Mg precipitation and increasing sodicity, it is worthwhile to focus on the further investigation around the potential effects of alkalinity on the soil properties such as organic matter and clay mineral dissolution, as described in the literature to be the major reasons for soil structural degradation as well as other soil properties that might be affected. This is important to establish appropriate and disciplined regulations in the Australian and New Zealand guidelines including an extensive range of soils.
- Investigation of soil chemical and hydraulic conductivity dynamic changes under application of alkaline and sodic irrigation water and followed by low electrolyte water (i.e. deionised water/rainwater). In addition, monitoring precipitation and dissolution processes of residual alkalinity during wetting and drying cycles which is envisaged to serve as diagnostic criterion for infiltration hazards in the field.

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Appendices

Appendix A. Critical flocculation concentration

Critical flocculation concentration (CFC) was determined for the selected soils to determine the flocculation power of cations. Figure A.1 and A.2 show the dialysis processes of soil clay and titration process, respectively, for Ca, Mg, Na and K tested on each selected soil. The flocculation power of each of these cations relative to Ca is presented in Table A.1.

Table A.1 Flocculation power for cations, relative to Ca.

Soil	*Na*	*K*	*Mg*	*Ca*
1	0.0378	0.0647	0.634	1
2	0.0373	0.0529	0.704	1
3	0.0436	0.0579	0.73	1
4	0.0368	0.0609	0.725	1
5	0.0454	0.0765	0.579	1
6	0.0247	0.0355	0.489	1
7	0.0428	0.0631	0.618	1
8	0.0372	0.0618	0.709	1
9	0.0734	0.0513	0.659	1
10	0.037	0.061	0.73	1
Average	0.0421	0.0583	0.6497	1
Min.	0.02	0.04	0.49	1
Max	0.07	0.08	0.73	1
StDev	0.013181	0.011257	0.079823	0

Figure A.1 Dialysis process of soil clays against deionised water to desalinize of clays and obtain external water electrical conductivity of 5.0 µS cm^{-1}.

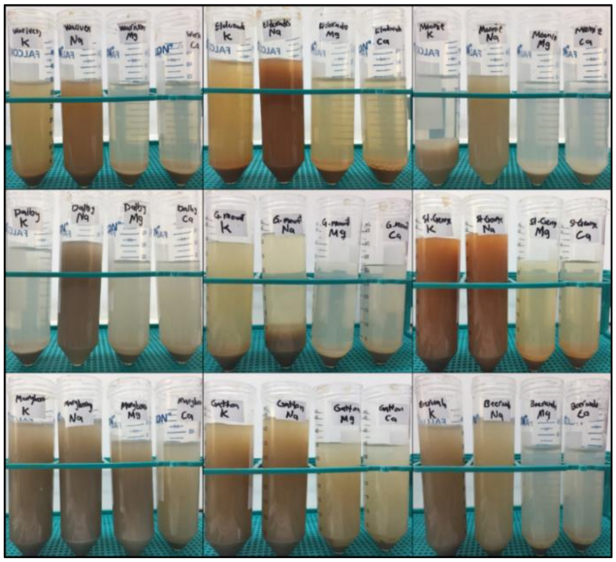

Figure A.2 Titration process to determine critical flocculation concentration for Ca, Mg, Na and K and determined for each selected soil.

Appendix B. pH buffering capacity

The pH buffering capacity of each soil was determined based on the method described in Nelson and Su (2010). The soil buffer was tested using HCl acid (-ve) and NaOH alkali (+ve) from pH of 4.5 to 11.5. The pH buffer curves and the relationship to the pH of each selected soil are presented in Figure B.1 and B.2.

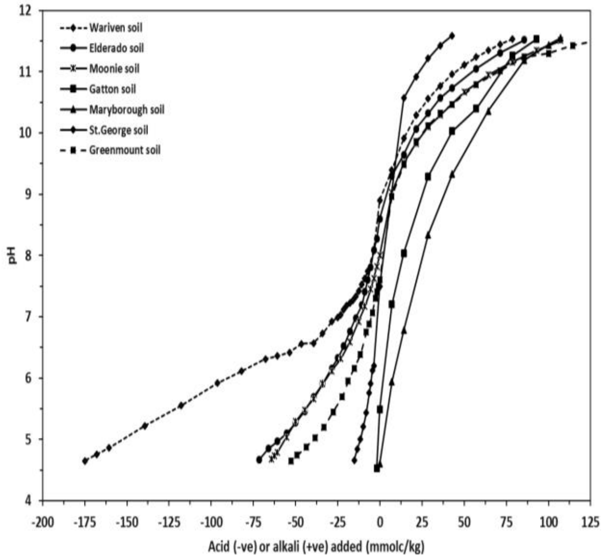

Figure B.1 pH buffer curves of soils. Points are experimental data and lines are fitted curves.

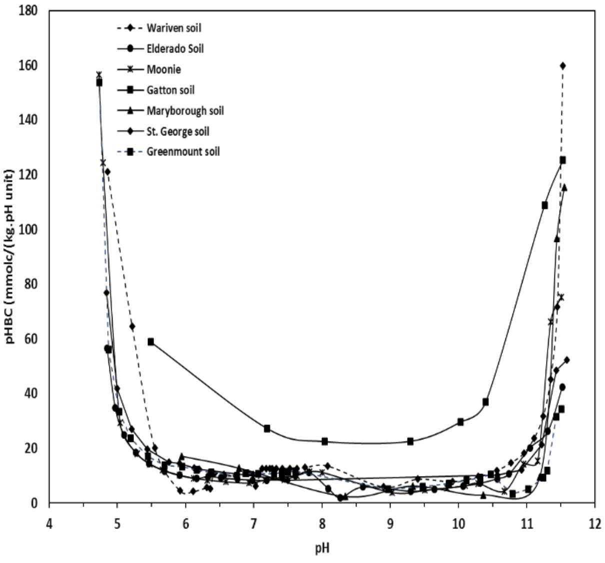

Figure B.2 The relationship between pH buffer capacity (pHBC) and pH of selected soil.

Appendix C. Soil water retention curve

Water retention curves were determined by the hanging water column for the selected soils. Air-dried soils were packed (65 cm^3, 2-cm height) in the sintered funnels at a bulk density similar to their natural state. The packed soils were equilibrated with water to reach saturation point (0 cm meters head), and samples were then subjected to negative pressure heads of 0–200 cm head (~0–20 kPa). The change in water content was logged that flowed out of the soil to hydraulic equilibrium is reached (Dane and Hopmans, 2002) for each negative pressure increments.

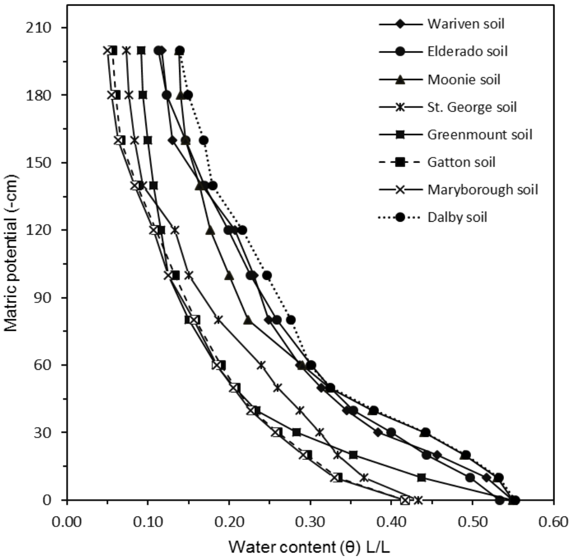

Figure C.1 Soil water retention curves for the selected soils using hanging columns method.

Figure C.2 Hanging column apparatus to determine soil water retention curve.

Appendix D. Long column experiment

Figure D.1 and D.2 demonstrate the long column experiment components and the application of the vacuum to the porous soil solution extraction tubes by extending the syringe plungers. The soil solution extraction tubes were installed on the targeted depths (5, 15, 25 and 35 cm) and soil moisture sensors were installed on the other side of columns at the same targeted depths.

Figure D.1 Long columns experimentation and major components.

Figure D.2 Long columns used for HYDRUS model validation.

D.1. Soil moisture meter

The soil moisture meter used in this experiment was assembled and coded by the student using different electronic parts from Australia and international markets. This soil moisture meter were calibrated using gravimetric water content determination (using oven method).

```
############## Soil moisture code for long columns##############
int sensorPin = A0;
int sensorValue = 0;
int percent = 0;
void setup() {
Serial.begin(9600);
}
void loop() {
sensorValue = analogRead(sensorPin);
percent = convertToPercent(sensorValue);
printValuesToSerial();
delay(1000);
}
int convertToPercent(int value)
{
int percentValue = 0;
percentValue = map(value, 550,0,0,100);
return percentValue;
}
void printValuesToSerial()
```

```
{
Serial.print("\n\nAnalog Value: ");
Serial.print(sensorValue);
Serial.print("\nPercent: ");
Serial.print(percent);
Serial.print("%");
}
```

D.2. Soil physical properties after dismantling high soil columns used for HYDRUS model evaluation.

The residual (θ_r) and saturated water (θ_s) content and bulk density of soil profiles used to determine effects of alkalinity of the soil physical and chemical properties and evaluation of HYDRUS model are presented in D.1. Statistical analysis of solution electrical conductivity, sodium adsorption ratio, pH and alkalinity (HCO_3^-) extracted at different depths for soil columns treated with irrigation water having 0, 98, 311, and 650 mg L^{-1} of HCO_3^- are presented in Table D.2, D.3, D.4, D.5, D.6.and D7.

Table D.1 Residual and saturated water content and bulk density of dismantled soil columns after experiment.

Irrigation alkalinity mg L^{-1}		***Soil 1***			***Soil 2***			***Soil 3***		
	Soil depth	θ_r	θ_s	***Bulk density (g cm^{-3})***	θ_r	θ_s	***Bulk density (g cm^{-3})***	θ_r	θ_s	***Bulk density (g cm^{-3})***
0	5	0.009	0.295	1.514	0.071	0.504	1.230	0.042	0.392	1.269
	15	0.010	0.301	1.484	0.059	0.446	1.260	0.058	0.362	1.288
	25	0.010	0.299	1.449	0.061	0.491	1.280	0.063	0.354	1.318
	35	0.012	0.307	1.461	0.064	0.459	1.317	0.056	0.334	1.297
98	5	0.012	0.262	1.582	0.051	0.455	1.239	0.035	0.361	1.305
	15	0.011	0.255	1.587	0.051	0.447	1.279	0.033	0.402	1.314
	25	0.009	0.273	1.601	0.052	0.430	1.279	0.032	0.387	1.251
	35	0.010	0.274	1.531	0.058	0.418	1.311	0.031	0.397	1.317
311	5	0.011	0.240	1.678	0.078	0.479	1.264	0.036	0.393	1.247
	15	0.012	0.258	1.567	0.060	0.433	1.255	0.037	0.402	1.335
	25	0.012	0.258	1.623	0.057	0.385	1.343	0.037	0.411	1.320
	35	0.009	0.263	1.612	0.061	0.411	1.301	0.035	0.406	1.281
650	5	0.010	0.225	1.645	0.071	0.435	1.289	0.046	0.401	1.285
	15	0.010	0.266	1.586	0.074	0.395	1.369	0.068	0.393	1.346
	25	0.011	0.276	1.531	0.078	0.406	1.309	0.051	0.397	1.339
	35	0.011	0.266	1.554	0.076	0.430	1.300	0.053	0.416	1.374

Table D.2 Statistical analysis of solution electrical conductivity, sodium adsorption ratio extracted at different depths for Soil 1 (Maryborough soil) columns and HYDRUS modelled results for 0, 98, 311, and 650 mg L^{-1} of HCO$_3^-$ irrigation waters.

soil depth (cm)		*Electrical conductivity (dS m^{-1}) of observed and HYDRUS predicted*																			
		Solution HCO$_3^-$= 0 (mg L^{-1})					*Solution HCO$_3^-$= 100 (mg L^{-1})*					*Solution HCO$_3^-$= 310 (mg L^{-1})*					*Solution HCO$_3^-$= 650 (mg L^{-1})*				
			days																		
		0	80	143	214	290	0	80	143	214	290	0	80	143	214	290	0	80	143	214	290
5	MAD	0.06	0.05	0.13	0.07	0.11	0.19	0.26	0.09	0.03	0.08	0.17	0.05	0.07	0.04	0.05	0.19	0.27	0.18	0.06	0.04
	MSE	0.00	0.00	0.02	0.01	0.01	0.04	0.09	0.01	0.00	0.01	0.04	0.00	0.01	0.00	0.00	0.05	0.10	0.04	0.00	0.00
	RMSE	0.06	0.05	0.14	0.07	0.12	0.21	0.30	0.10	0.03	0.09	0.19	0.05	0.07	0.04	0.05	0.22	0.32	0.20	0.06	0.04
	MAPE	3.52	2.85	6.72	4.31	6.86	8.11	13.38	5.43	1.59	5.11	10.69	2.47	3.47	2.01	2.74	11.90	16.43	9.81	3.01	2.17
	I_A	0.97	1.00	0.88	0.96	0.92	0.80	0.98	0.93	0.99	0.95	0.84	1.00	0.95	0.99	0.98	0.80	0.98	0.82	0.97	0.98
15	MAD	0.03	0.14	0.06	0.04	0.18	0.06	0.02	0.03	0.06	0.07	0.23	0.03	0.12	0.09	0.03	0.45	0.21	0.07	0.03	0.20
	MSE	0.00	0.02	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.01	0.07	0.00	0.02	0.01	0.00	0.29	0.06	0.00	0.00	0.05
	RMSE	0.03	0.15	0.06	0.04	0.20	0.06	0.03	0.03	0.06	0.07	0.27	0.04	0.13	0.09	0.04	0.54	0.24	0.07	0.03	0.22
	MAPE	1.80	8.58	3.17	2.46	11.94	3.28	1.19	2.01	3.55	4.27	15.08	1.69	5.74	4.32	1.70	29.20	11.29	3.54	1.57	8.67
	I_A	0.99	0.99	0.97	0.99	0.83	0.97	1.00	0.99	0.97	0.98	0.75	1.00	0.91	0.94	0.99	0.54	0.99	0.97	0.99	0.84
25	MAD	0.07	0.03	0.18	0.15	0.14	0.10	0.23	0.05	0.01	0.08	0.23	0.03	0.05	0.02	0.06	0.22	0.49	0.11	0.06	0.11
	MSE	0.00	0.00	0.04	0.03	0.02	0.01	0.07	0.00	0.00	0.01	0.07	0.00	0.00	0.00	0.00	0.07	0.34	0.01	0.00	0.01
	RMSE	0.07	0.03	0.20	0.16	0.15	0.11	0.27	0.05	0.02	0.08	0.27	0.03	0.05	0.03	0.06	0.26	0.59	0.12	0.06	0.12
	MAPE	3.65	1.52	8.83	9.37	8.85	5.37	12.91	3.24	0.89	4.69	13.55	1.60	2.24	1.20	3.19	13.82	26.93	6.01	2.89	4.97
	I_A	0.97	1.00	0.85	0.88	0.89	0.93	0.98	0.99	1.00	0.95	0.75	1.00	0.98	0.99	0.97	0.76	0.94	0.95	0.97	0.92
35	MAD	0.22	0.13	0.32	0.14	0.03	0.12	0.08	0.27	0.08	0.10	0.12	0.12	0.10	0.03	0.18	0.21	0.62	0.30	0.12	0.32
	MSE	0.06	0.02	0.14	0.03	0.00	0.02	0.01	0.10	0.01	0.01	0.02	0.02	0.01	0.00	0.04	0.06	0.56	0.12	0.02	0.13
	RMSE	0.24	0.15	0.37	0.16	0.03	0.12	0.08	0.31	0.08	0.11	0.13	0.13	0.11	0.03	0.20	0.24	0.75	0.35	0.13	0.37
	MAPE	9.00	8.00	14.27	8.81	1.70	5.09	3.85	15.72	4.68	5.92	4.77	5.73	5.48	1.35	7.82	10.35	32.73	16.13	6.15	12.85
	I_A	0.82	0.99	0.72	0.89	0.99	0.93	1.00	0.77	0.96	0.93	0.93	1.00	0.94	0.99	0.85	0.82	0.88	0.73	0.91	0.72
		Sodium adsorption ratio (mol$^{0.5}$ L$^{-1.5}$) of observed and HYDRUS predicted																			
5	MAD	0.11	0.86	1.33	1.51	0.99	3.15	1.88	3.48	1.46	1.81	3.01	0.85	0.88	1.28	3.36	0.17	3.62	1.78	3.53	0.71
	MSE	0.02	0.93	2.35	3.03	1.20	13.83	4.63	16.96	2.70	4.30	12.74	0.84	0.92	2.04	15.66	0.03	18.32	4.09	17.23	0.52
	RMSE	0.14	0.97	1.53	1.74	1.10	3.72	2.15	4.12	1.64	2.07	3.57	0.92	0.96	1.43	3.96	0.19	4.28	2.02	4.15	0.72
	MAPE	1.19	8.96	13.65	15.13	7.43	27.18	13.21	28.90	9.61	12.91	31.27	6.31	6.67	8.12	18.03	2.39	27.59	11.22	22.55	3.10
	I_A	0.95	0.99	0.31	0.49	0.56	0.10	0.97	0.11	0.50	0.45	0.09	0.99	0.54	0.50	0.33	0.97	0.96	0.24	0.34	0.68
15	MAD	0.08	1.29	1.73	0.73	0.49	0.87	6.24	6.40	3.97	3.38	0.89	4.48	4.68	3.15	3.64	0.56	3.95	3.76	3.63	3.10
	MSE	0.01	2.26	4.14	0.64	0.26	1.04	56.75	59.57	22.26	15.88	1.10	29.03	31.62	13.62	18.36	0.43	22.45	19.85	18.25	12.88
	RMSE	0.11	1.50	2.03	0.80	0.51	1.02	7.53	7.72	4.72	3.98	1.05	5.39	5.62	3.69	4.29	0.66	4.74	4.45	4.27	3.59
	MAPE	1.09	16.85	22.49	6.95	4.17	21.87	100.10	93.65	34.26	24.63	26.80	71.48	59.75	16.51	18.57	28.02	51.71	30.16	24.36	15.81
	I_A	0.97	0.98	0.46	0.67	0.80	0.45	0.77	0.27	0.32	0.35	0.43	0.87	0.30	0.34	0.32	0.61	0.94	0.33	0.34	0.36
25	MAD	0.16	0.33	0.75	1.55	0.87	0.93	0.92	2.64	0.30	1.18	0.84	0.39	0.81	0.56	1.98	0.67	3.24	1.43	2.04	2.01
	MSE	0.03	0.12	0.71	3.20	0.93	1.22	1.14	9.98	0.09	1.75	1.00	0.18	0.85	0.35	5.29	0.62	15.23	2.62	5.40	5.17
	RMSE	0.16	0.34	0.84	1.79	0.96	1.11	1.07	3.16	0.30	1.32	1.00	0.43	0.92	0.59	2.30	0.79	3.90	1.62	2.32	2.27
	MAPE	2.41	4.43	9.45	12.70	7.11	30.86	17.81	43.98	2.48	9.18	30.61	7.23	11.68	4.45	16.61	31.39	36.49	9.67	11.69	10.38
	I_A	0.93	1.00	0.66	0.46	0.60	0.41	0.99	0.38	0.89	0.55	0.45	1.00	0.63	0.71	0.43	0.54	0.96	0.48	0.43	0.44
35	MAD	0.03	1.45	1.10	2.39	1.54	0.86	0.70	0.35	0.67	0.96	0.59	1.72	2.43	4.37	1.01	0.37	2.15	3.83	2.35	1.68
	MSE	0.00	2.95	1.64	7.98	3.17	1.03	0.65	0.15	0.55	1.14	0.47	4.23	8.50	27.54	1.31	0.19	6.69	21.38	7.46	3.59

	RMSE	0.05	1.72	1.28	2.83	1.78	1.01	0.81	0.38	0.74	1.07	0.69	2.06	2.91	5.25	1.14	0.43	2.59	4.62	2.73	1.89
	MAPE	0.84	30.15	18.84	20.06	12.98	26.06	13.02	5.81	7.33	8.00	17.09	26.99	30.74	32.89	8.80	23.65	36.65	40.16	17.40	10.20
	I_A	0.99	0.97	0.56	0.38	0.46	0.45	0.99	0.82	0.67	0.57	0.61	0.94	0.38	0.30	0.56	0.75	0.98	0.32	0.40	0.47

Table D.3 Statistical analysis of solution pH, alkalinity (HCO_3^-) extracted at different depths for Soil 1 (Maryborough soil) columns and HYDRUS modelled results for 0, 98, 311, and 650 mg L^{-1} of HCO_3^- irrigation waters.

soil depth (cm)		*Solution pH of observed and HYDRUS predicted*																			
		Solution HCO_3^-= 0 (mg L^{-1})					*Solution HCO_3^-= 100 (mg L^{-1})*					*Solution HCO_3^-= 310 (mg L^{-1})*					*Solution HCO_3^-= 650 (mg L^{-1})*				
			days																		
		0	80	143	214	290	0	80	143	214	290	0	80	143	214	290	0	80	143	214	290
5	MAD	0.49	0.18	0.63	0.09	0.61	0.53	0.34	0.91	0.35	1.20	0.95	1.47	1.51	1.53	0.32	1.80	1.48	1.41	0.55	0.83
	MSE	0.31	0.03	0.52	0.01	0.49	0.37	0.14	1.13	0.14	2.00	1.25	3.05	3.19	3.29	0.11	4.63	3.04	2.73	0.37	0.89
	RMSE	0.55	0.18	0.72	0.09	0.70	0.61	0.37	1.06	0.37	1.41	1.12	1.75	1.79	1.81	0.33	2.15	1.74	1.65	0.61	0.94
	MAPE	9.74	3.66	13.83	1.52	12.30	11.78	7.10	20.19	6.07	25.05	21.04	29.45	30.04	30.72	4.64	29.28	23.82	22.14	7.26	11.48
	I_A	0.52	1.00	0.40	0.95	0.58	0.50	1.00	0.23	0.74	0.43	0.36	0.91	0.09	0.38	0.78	0.34	0.90	0.25	0.73	0.63
15	MAD	0.60	0.32	0.25	1.06	0.42	0.41	0.34	0.16	0.61	0.42	0.89	0.74	1.50	1.00	0.91	1.19	0.90	1.87	0.80	1.01
	MSE	0.48	0.12	0.07	1.57	0.23	0.22	0.15	0.03	0.50	0.22	1.12	0.75	3.18	1.35	1.10	2.03	1.08	4.93	0.81	1.36
	RMSE	0.69	0.35	0.27	1.25	0.48	0.47	0.38	0.16	0.71	0.47	1.06	0.87	1.78	1.16	1.05	1.42	1.04	2.22	0.90	1.16
	MAPE	13.35	7.06	5.58	18.21	8.63	10.08	7.93	3.71	12.00	8.68	21.33	14.63	31.05	17.73	15.72	25.77	15.53	31.40	10.46	13.92
	I_A	0.46	0.99	0.78	0.44	0.83	0.58	0.99	0.88	0.56	0.62	0.37	0.98	0.39	0.47	0.48	0.42	0.98	0.44	0.64	0.58
25	MAD	0.49	0.11	0.29	0.63	0.46	0.38	0.09	0.56	0.09	0.48	0.78	1.61	0.14	0.25	0.24	0.80	2.23	0.32	0.06	0.34
	MSE	0.32	0.01	0.10	0.53	0.27	0.19	0.01	0.41	0.01	0.29	0.86	3.72	0.02	0.07	0.06	0.89	7.20	0.11	0.01	0.13
	RMSE	0.56	0.11	0.32	0.73	0.52	0.43	0.09	0.64	0.09	0.54	0.93	1.93	0.14	0.26	0.25	0.95	2.68	0.34	0.10	0.36
	MAPE	10.81	2.39	6.89	11.08	8.38	9.49	2.01	13.05	1.76	9.98	19.18	30.96	2.92	4.54	4.06	18.96	37.75	5.33	0.90	4.94
	I_A	0.52	1.00	0.72	0.55	0.63	0.60	1.00	0.68	0.95	0.64	0.40	0.86	0.99	0.82	0.83	0.53	0.85	0.86	0.98	0.85
35	MAD	0.41	0.89	1.02	1.59	1.40	0.40	1.09	0.58	1.00	0.68	0.88	1.73	1.49	1.49	1.45	0.92	2.25	2.13	1.23	1.67
	MSE	0.22	1.11	1.46	3.60	2.79	0.20	1.67	0.46	1.40	0.62	1.09	4.33	3.18	3.15	2.96	1.19	7.35	6.54	2.04	3.86
	RMSE	0.47	1.05	1.21	1.90	1.67	0.45	1.29	0.67	1.18	0.79	1.04	2.08	1.78	1.77	1.72	1.09	2.71	2.56	1.43	1.96
	MAPE	9.93	20.17	21.63	28.15	25.75	9.67	23.06	13.78	19.06	13.44	21.33	33.79	29.35	24.72	23.33	21.79	40.21	33.16	17.12	24.92
	I_A	0.63	0.95	0.45	0.37	0.39	0.64	0.92	0.57	0.45	0.53	0.41	0.76	0.38	0.38	0.38	0.48	0.88	0.40	0.53	0.46
		Solution alkalinity (HCO_3^-) of observed and HYDRUS predicted																			
5	MAD	0.00	0.44	0.54	0.27	0.51	0.12	0.10	0.04	0.17	0.07	0.12	4.22	3.96	4.37	4.10	0.03	5.15	5.65	3.76	1.73
	MSE	0.00	0.28	0.43	0.11	0.38	0.02	0.02	0.00	0.04	0.01	0.02	26.36	23.	28.30	24.8	0.00	39.31	47.25	20	4.17
	RMSE	0.00	0.53	0.66	0.33	0.62	0.15	0.13	0.05	0.21	0.08	0.14	5.13	4.81	5.32	4.98	0.04	6.27	6.87	4.54	2.04
	MAPE	–	–	–	–	–	67.5	–	22.5	55.4	13.9	67.5	25	43	15	57	4.7	14	78.6	10.4	25.8
	I_A	1.00	0.33	0.39	0.75	0.60	0.88	0.98	0.98	0.84	0.96	0.89	0.31	0.14	0.26	0.26	0.99	0.48	0.15	0.27	0.37
15	MAD	0.00	0.15	0.41	0.44	0.42	0.01	0.00	0.01	0.06	0.05	0.08	0.07	1.54	1.69	1.69	0.00	1.68	5.83	3.26	3.23
	MSE	0.00	0.03	0.24	0.29	0.26	0.00	0.00	0.00	0.01	0.00	0.01	0.01	3.51	4.24	4.24	0.00	4.18	50.21	15.45	15.10
	RMSE	0.00	0.19	0.49	0.54	0.51	0.02	0.00	0.02	0.07	0.06	0.09	0.08	1.87	2.06	2.06	0.00	2.05	7.09	3.93	3.89
	MAPE	–	–	–	–	–	68	–	68	68	22	68	68	85	62	61	–	78	12	75	73
	I_A	1.00	0.95	0.66	0.64	0.64	1.00	1.00	1.00	0.96	1.00	0.94	1.00	0.38	0.36	0.22	1.00	0.95	0.24	0.29	0.13
25	MAD	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.03	0.07	0.10	0.27	0.00	0.00	1.32	3.34	0.00	0.44	3.79	2.37	3.07

	MSE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.11	0.00	0.00	2.59	16.55	0.00	0.28	21.21	8.06	13.61
	RMSE	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.04	0.08	0.12	0.33	0.00	0.00	1.61	4.07	0.00	0.53	4.61	2.84	3.69
	MAPE	–	–	–	–	–	–	–	–	–	–	67.51	–	–	–	–	–	67.51	86	51.86	66.3
	I_A	1.00	1.00	0.99	1.00	1.00	1.00	1.00	0.99	0.96	0.92	0.70	1.00	1.00	0.40	0.28	1.00	1.00	0.21	0.32	0.29
35	MAD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.24	0.00	0.00	0.16	0.43	0.00	0.20	0.35	1.77	3.24
	MSE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.00	0.00	0.04	0.27	0.00	0.06	0.18	4.47	15.23
	RMSE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.30	0.00	0.00	0.20	0.52	0.00	0.24	0.43	2.11	3.90
	MAPE	–	–	–	–	–	–	–	–	–	–	67.51	–	–	67.51	67.51	–	67.51	67.51	41.18	74.41
	I_A	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.77	1.00	1.00	0.85	0.64	1.00	1.00	0.69	0.36	0.29

Table D.4 Statistical analysis of solution electrical conductivity, sodium adsorption ratio extracted at different depths for Soil 2 (Yarrandoo soil) columns and HYDRUS modelled results for 0, 98, 311, and 650 mg L^{-1} of HCO_3^- irrigation waters.

Soil depth (cm)		*Electrical conductivity (dS m^{-1}) of observed and HYDRUS predicted*																			
		Solution HCO_3^-= 0 (mg L^{-1})					*Solution HCO_3^-= 100 (mg L^{-1})*					*Solution HCO_3^-= 310 (mg L^{-1})*					*Solution HCO_3^-= 650 (mg L^{-1})*				
			days																		
		0	80	143	214	290	0	80	143	214	290	0	80	143	214	290	0	80	143	214	290
5	MAD	0.05	0.19	0.06	0.10	0.15	0.10	0.10	0.18	0.13	0.32	0.07	0.15	0.12	0.13	0.24	0.05	0.19	0.11	0.03	0.08
	MSE	0.00	0.05	0.00	0.01	0.03	0.01	0.01	0.04	0.02	0.14	0.00	0.03	0.02	0.02	0.08	0.00	0.04	0.01	0.00	0.01
	RMSE	0.05	0.22	0.06	0.10	0.16	0.11	0.11	0.21	0.15	0.37	0.07	0.17	0.13	0.15	0.27	0.05	0.21	0.12	0.03	0.08
	MAPE	3.19	9.66	3.16	5.24	7.70	4.74	5.16	9.18	7.06	14.73	3.32	7.89	6.16	7.03	11.88	1.71	8.70	6.36	1.39	4.11
	I_A	0.97	0.99	0.97	0.94	0.88	0.93	1.00	0.81	0.89	0.72	0.97	0.99	0.90	0.90	0.79	0.98	0.99	0.91	0.99	0.95
15	MAD	0.05	0.43	0.11	0.08	0.20	0.20	0.06	0.17	0.18	0.42	0.07	0.14	0.31	0.41	0.22	0.03	0.05	0.05	0.08	0.19
	MSE	0.00	0.25	0.01	0.01	0.05	0.05	0.00	0.03	0.04	0.25	0.01	0.02	0.13	0.23	0.06	0.00	0.00	0.00	0.01	0.04
	RMSE	0.05	0.50	0.11	0.08	0.23	0.22	0.06	0.18	0.20	0.50	0.07	0.16	0.36	0.48	0.25	0.03	0.05	0.05	0.09	0.21
	MAPE	2.62	17.13	5.04	3.89	9.65	7.97	2.80	7.59	8.18	17.07	3.71	6.82	13.79	17.04	10.80	1.12	2.52	2.52	4.18	8.53
	I_A	0.98	0.96	0.93	0.96	0.83	0.81	1.00	0.86	0.85	0.62	0.96	1.00	0.73	0.66	0.79	0.99	1.00	0.98	0.95	0.87
25	MAD	0.09	0.55	0.37	0.27	0.23	0.30	0.03	0.18	0.29	0.55	0.14	0.10	0.36	0.37	0.18	0.04	0.65	0.11	0.24	0.17
	MSE	0.01	0.43	0.19	0.10	0.07	0.11	0.00	0.04	0.11	0.42	0.02	0.01	0.18	0.19	0.04	0.00	0.61	0.01	0.08	0.04
	RMSE	0.09	0.66	0.43	0.31	0.26	0.34	0.04	0.20	0.33	0.65	0.16	0.11	0.42	0.43	0.20	0.04	0.78	0.12	0.28	0.19
	MAPE	6.23	22.37	15.72	12.45	10.49	7.65	1.02	7.54	11.95	19.86	7.13	4.88	14.86	15.50	8.56	2.86	46.64	5.26	10.43	7.85
	I_A	0.94	0.93	0.63	0.76	0.79	0.70	1.00	0.88	0.75	0.58	0.88	1.00	0.64	0.68	0.85	0.99	0.89	0.97	0.78	0.85
35	MAD	0.28	0.23	0.15	0.33	0.51	0.43	0.07	0.08	0.49	0.84	0.24	0.29	0.55	0.61	0.71	0.19	0.07	0.04	0.05	0.42
	MSE	0.10	0.07	0.03	0.14	0.36	0.24	0.01	0.01	0.33	0.99	0.07	0.11	0.43	0.52	0.70	0.05	0.00	0.00	0.00	0.24
	RMSE	0.31	0.26	0.16	0.38	0.60	0.49	0.07	0.09	0.57	1.00	0.27	0.34	0.66	0.72	0.84	0.21	0.07	0.04	0.05	0.49
	MAPE	8.75	9.16	5.77	13.29	20.09	14.02	2.19	3.28	17.34	25.79	8.56	11.52	19.70	21.66	24.21	7.95	3.32	1.53	2.42	16.07
	I_A	0.76	0.99	0.88	0.71	0.60	0.60	1.00	0.95	0.62	0.49	0.80	0.98	0.58	0.56	0.53	0.85	1.00	0.99	0.98	0.65
		Sodium adsorption ratio ($mol^{0.5}$ $L^{-1.5}$) of observed and HYDRUS predicted																			
5	MAD	0.18	1.68	0.87	0.21	0.21	0.03	0.78	0.49	0.41	0.91	0.55	0.61	0.72	1.15	0.61	0.22	0.39	1.44	1.63	0.59
	MSE	0.03	3.95	0.97	0.04	0.04	0.00	0.82	0.28	0.19	1.07	0.40	0.50	0.67	1.79	0.46	0.06	0.18	2.83	3.59	0.38
	RMSE	0.19	1.99	0.99	0.21	0.21	0.05	0.90	0.53	0.44	1.03	0.63	0.71	0.82	1.34	0.68	0.23	0.42	1.68	1.90	0.62
	MAPE	2.07	26.36	11.30	2.41	2.32	0.86	14.78	6.96	5.07	10.94	13.88	13.80	10.25	13.54	6.82	4.68	5.91	15.25	13.62	4.80
	I_A	0.93	0.64	0.62	0.90	0.97	0.69	0.73	0.71	0.87	0.68	0.16	0.20	0.15	0.16	0.11	0.92	0.85	0.60	0.61	0.84

15	MAD	0.08	1.80	1.44	0.87	1.41	0.08	0.10	0.22	1.35	1.31	0.08	0.11	0.35	1.26	1.37	0.11	0.08	0.09	2.14	2.28
	MSE	0.01	4.71	2.99	1.03	2.77	0.01	0.01	0.06	2.57	2.40	0.01	0.01	0.16	2.25	2.65	0.01	0.01	0.01	6.60	7.48
	RMSE	0.09	2.17	1.73	1.01	1.66	0.08	0.10	0.24	1.60	1.55	0.08	0.12	0.40	1.50	1.63	0.11	0.08	0.09	2.57	2.74
	MAPE	1.49	69.46	45.61	13.35	19.01	3.34	3.52	6.52	23.89	20.84	2.36	3.60	9.78	23.93	22.74	2.61	1.96	2.43	29.66	29.01
	I_A	1.00	0.85	0.94	0.96	0.89	1.00	1.00	1.00	0.95	0.94	1.00	1.00	1.00	0.96	0.95	0.99	1.00	1.00	0.95	0.95
25	MAD	0.04	0.59	0.46	1.33	1.90	0.06	0.02	0.08	0.76	1.08	0.02	0.22	0.34	0.62	0.39	0.06	0.33	0.45	0.71	1.63
	MSE	0.00	0.48	0.29	2.53	5.22	0.00	0.00	0.01	0.82	1.67	0.00	0.06	0.15	0.53	0.20	0.00	0.15	0.28	0.70	3.81
	RMSE	0.05	0.69	0.54	1.59	2.29	0.06	0.03	0.08	0.91	1.29	0.03	0.25	0.39	0.73	0.45	0.06	0.38	0.53	0.83	1.95
	MAPE	1.28	25.34	17.90	25.50	30.98	2.70	0.98	3.52	21.87	25.61	1.07	10.41	15.78	16.91	11.22	2.99	14.74	19.46	16.89	28.08
	I_A	1.00	0.99	1.00	0.97	0.92	1.00	1.00	1.00	0.99	0.98	1.00	1.00	1.00	0.99	1.00	1.00	1.00	1.00	1.00	0.98
35	MAD	0.04	0.74	0.73	0.43	1.07	0.03	0.06	0.15	0.63	0.52	0.03	0.04	0.02	0.26	0.45	0.04	0.03	0.03	0.92	1.22
	MSE	0.00	0.77	0.75	0.24	1.63	0.00	0.00	0.03	0.56	0.38	0.00	0.00	0.00	0.09	0.27	0.00	0.00	0.00	1.20	2.13
	RMSE	0.05	0.88	0.86	0.49	1.28	0.03	0.07	0.17	0.75	0.61	0.03	0.04	0.03	0.29	0.52	0.04	0.03	0.04	1.09	1.46
	MAPE	1.32	35.91	35.96	11.73	23.24	1.84	3.40	7.11	21.49	18.13	1.24	1.94	1.13	10.32	15.06	2.10	1.39	1.78	26.91	29.62
	I_A	1.00	0.99	0.99	1.00	0.98	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.99

Table D.5 Statistical analysis of solution pH, alkalinity (HCO_3^-) extracted at different depths for Soil 2 (Yarrandoo soil) columns and HYDRUS modelled results for 0, 98, 311, and 650 mg L^{-1} of HCO_3^- irrigation waters.

Soil depth (cm)		***Solution pH of observed and HYDRUS predicted***																			
		Solution HCO_3^-= 0 (mg L^{-1})					***Solution HCO_3^-= 100 (mg L^{-1})***					***Solution HCO_3^-= 310 (mg L^{-1})***					***Solution HCO_3^-= 650 (mg L^{-1})***				
			days																		
		0	**80**	**143**	**214**	**290**	**0**	**80**	**143**	**214**	**290**	**0**	**80**	**143**	**214**	**290**	**0**	**80**	**143**	**214**	**290**
5	MAD	1.42	0.84	0.25	0.94	0.97	0.30	0.63	0.43	0.54	0.75	0.24	0.19	0.99	1.06	1.43	0.71	1.04	0.82	0.91	0.88
	MSE	2.76	0.92	0.07	1.16	1.24	0.09	0.49	0.22	0.35	0.73	0.06	0.04	1.28	1.49	2.77	0.63	1.41	0.84	1.06	1.00
	RMSE	1.66	0.96	0.26	1.08	1.11	0.31	0.70	0.46	0.59	0.85	0.24	0.19	1.13	1.22	1.66	0.79	1.19	0.92	1.03	1.00
	MAPE	21.13	11.94	3.46	13.91	14.16	4.08	8.28	5.53	6.96	10.21	3.12	2.48	12.65	13.39	17.78	9.03	13.28	10.01	11.31	10.94
	I_A	0.25	0.97	0.89	0.60	0.59	0.86	0.99	0.76	0.74	0.65	0.87	1.00	0.43	0.57	0.50	0.58	0.98	0.52	0.61	0.62
15	MAD	1.08	0.83	0.44	0.72	0.89	0.11	0.96	0.61	0.61	0.48	0.19	1.11	1.10	1.44	1.02	0.84	1.04	1.02	1.11	0.91
	MSE	1.57	0.89	0.22	0.67	1.05	0.02	1.22	0.45	0.46	0.27	0.04	1.64	1.61	2.83	1.35	0.91	1.42	1.37	1.63	1.07
	RMSE	1.25	0.94	0.47	0.82	1.02	0.12	1.10	0.67	0.68	0.52	0.19	1.28	1.27	1.68	1.16	0.95	1.19	1.17	1.28	1.03
	MAPE	15.70	11.56	5.92	10.30	12.91	1.55	12.87	7.74	7.85	5.98	2.55	14.45	14.41	18.62	12.47	11.01	13.56	13.09	14.41	11.39
	I_A	0.38	0.98	0.80	0.66	0.61	0.96	0.98	0.71	0.71	0.78	0.90	0.98	0.56	0.50	0.58	0.50	0.98	0.58	0.56	0.61
25	MAD	0.95	0.78	0.52	0.43	0.63	0.16	0.76	0.75	0.79	0.62	0.13	0.57	0.99	0.96	1.12	0.71	0.88	1.03	1.02	0.90
	MSE	1.20	0.78	0.33	0.21	0.49	0.03	0.73	0.71	0.80	0.47	0.02	0.38	1.29	1.19	1.66	0.64	1.01	1.40	1.36	1.05
	RMSE	1.10	0.88	0.57	0.46	0.70	0.16	0.86	0.84	0.90	0.68	0.13	0.62	1.13	1.09	1.29	0.80	1.01	1.18	1.17	1.02
	MAPE	13.64	10.92	7.21	6.11	9.09	2.25	9.86	9.69	10.49	7.94	1.74	7.02	12.68	12.11	13.79	9.25	11.60	13.42	13.07	11.31
	I_A	0.44	0.98	0.75	0.80	0.70	0.94	0.99	0.66	0.64	0.71	0.95	1.00	0.59	0.59	0.56	0.57	0.99	0.57	0.58	0.61
35	MAD	1.07	1.05	1.07	1.07	1.08	0.26	0.78	0.74	0.77	0.66	0.11	0.84	0.99	1.00	0.88	0.97	0.67	0.89	1.06	0.84
	MSE	1.54	1.47	1.53	1.52	1.55	0.07	0.77	0.70	0.76	0.54	0.01	0.91	1.28	1.30	1.00	1.23	0.56	1.01	1.48	0.89
	RMSE	1.24	1.21	1.24	1.23	1.25	0.27	0.88	0.83	0.87	0.73	0.12	0.96	1.13	1.14	1.00	1.11	0.75	1.01	1.21	0.94
	MAPE	15.55	14.84	14.79	14.96	15.34	3.86	10.17	9.59	10.11	8.52	1.51	10.94	12.96	12.72	10.96	13.18	8.58	11.52	13.79	10.38
	I_A	0.38	0.97	0.56	0.57	0.56	0.88	0.99	0.66	0.65	0.69	0.96	0.99	0.59	0.58	0.62	0.44	0.99	0.61	0.57	0.63

		Solution alkalinity (HCO$_3^-$) of observed and HYDRUS predicted																			
5	MAD	0.55	1.10	0.83	0.63	0.54	0.12	0.43	0.29	0.29	0.27	0.15	0.98	1.73	1.41	1.43	0.18	4.08	3.68	3.29	3.21
	MSE	0.43	1.77	1.00	0.58	0.42	0.02	0.26	0.11	0.12	0.10	0.03	1.37	4.32	2.84	2.90	0.04	24.23	19.60	15.56	14.86
	RMSE	0.66	1.33	1.00	0.76	0.65	0.14	0.51	0.33	0.34	0.32	0.16	1.17	2.08	1.69	1.70	0.20	4.92	4.43	3.94	3.85
	MAPE	96.7	167.3	110.	123.9	110.9	10.28	35.96	21.05	21.63	19.95	6.02	37.36	75.44	45.14	44.79	4.97	90.11	69.62	55.86	53.61
	I_A	0.60	0.46	0.43	0.68	0.72	0.90	0.93	0.67	0.75	0.76	0.86	0.95	0.09	0.40	0.39	0.81	0.77	0.14	0.29	0.29
15	MAD	0.44	0.61	1.41	1.18	0.79	0.05	1.46	0.80	0.86	1.02	0.13	0.61	0.25	0.30	0.62	0.23	2.88	3.86	2.74	2.72
	MSE	0.27	0.53	2.90	2.01	0.91	0.00	3.08	0.90	1.07	1.51	0.02	0.51	0.07	0.11	0.52	0.06	12.04	21.69	10.69	10.52
	RMSE	0.52	0.73	1.70	1.42	0.95	0.05	1.75	0.95	1.03	1.23	0.14	0.71	0.27	0.33	0.72	0.25	3.47	4.66	3.27	3.24
	MAPE	49.51	49.54	90.35	86.62	58.41	3.23	33.47	27.25	29.08	31.99	5.36	20.00	6.92	6.56	13.37	6.22	75.76	80.71	40.77	40.21
	I_A	0.69	0.94	0.49	0.53	0.62	0.98	0.91	0.50	0.48	0.74	0.88	0.98	0.80	0.74	0.84	0.75	0.89	0.27	0.31	0.44
25	MAD	0.40	0.30	0.56	0.41	0.54	0.10	2.04	1.69	1.24	1.30	0.08	1.15	0.39	0.11	0.14	0.09	0.22	2.34	3.18	3.17
	MSE	0.23	0.12	0.42	0.23	0.41	0.01	6.07	4.16	2.21	2.47	0.01	1.89	0.19	0.01	0.02	0.01	0.05	7.82	14.54	14.45
	RMSE	0.48	0.35	0.65	0.48	0.64	0.11	2.46	2.04	1.49	1.57	0.08	1.37	0.44	0.11	0.14	0.09	0.23	2.80	3.81	3.80
	MAPE	39.73	16.90	21.52	20.63	27.02	6.05	39.65	37.12	34.63	35.90	3.60	28.53	8.81	2.73	3.20	3.43	5.01	45.92	54.47	52.52
	I_A	0.72	0.98	0.72	0.79	0.72	0.93	0.87	0.30	0.41	0.40	0.95	0.90	0.90	0.93	0.90	0.95	1.00	0.31	0.29	0.29
35	MAD	0.51	0.57	0.05	0.70	0.75	0.28	0.35	1.16	1.21	1.41	0.07	1.06	1.15	1.01	1.00	0.08	0.71	0.23	1.69	2.47
	MSE	0.37	0.46	0.00	0.69	0.80	0.11	0.16	1.92	2.12	2.91	0.01	1.62	1.89	1.41	1.40	0.01	0.70	0.06	3.97	8.61
	RMSE	0.61	0.68	0.05	0.83	0.90	0.33	0.40	1.39	1.46	1.71	0.07	1.27	1.37	1.19	1.18	0.08	0.83	0.25	1.99	2.94
	MAPE	50.05	18.04	1.89	22.03	24.88	16.14	20.34	29.99	32.98	37.50	3.74	26.82	24.79	18.61	18.21	2.76	17.92	4.99	24.88	35.48
	I_A	0.63	0.95	0.99	0.65	0.63	0.73	0.97	0.42	0.41	0.39	0.97	0.92	0.42	0.45	0.45	0.96	0.99	0.83	0.37	0.32

Table D.6 Statistical analysis of solution electrical conductivity, sodium adsorption ratio extracted at different depths for Soil 3 (Eldorado soil) columns and HYDRUS modelled results for 0, 98, 311, and 650 mg L^{-1} of HCO$_3^-$ irrigation waters.

Soil depth (cm)		Electrical conductivity (dS m^{-1}) of observed and HYDRUS predicted																			
		Solution HCO$_3^-$= 0 (mg L^{-1})					Solution HCO$_3^-$= 100 (mg L^{-1})					Solution HCO$_3^-$= 310 (mg L^{-1})					Solution HCO$_3^-$= 650 (mg L^{-1})				
			days																		
		0	80	143	214	290	0	80	143	214	290	0	80	143	214	290	0	80	143	214	290
5	MAD	0.12	0.09	0.15	0.23	0.21	0.06	0.28	0.04	0.14	0.20	0.11	0.09	0.03	0.10	0.22	0.07	0.46	0.14	0.08	0.10
	MSE	0.02	0.01	0.03	0.07	0.06	0.00	0.10	0.00	0.02	0.05	0.02	0.01	0.00	0.01	0.07	0.01	0.30	0.02	0.01	0.01
	RMSE	0.13	0.10	0.17	0.26	0.24	0.07	0.32	0.04	0.15	0.23	0.12	0.10	0.04	0.11	0.26	0.08	0.55	0.15	0.08	0.11
	MAPE	6.70	4.84	10.06	10.73	10.57	1.61	12.37	2.34	7.22	10.17	5.54	5.22	2.09	5.71	11.53	4.33	19.88	7.56	4.48	5.78
	I_A	0.89	1.00	0.86	0.80	0.81	0.96	0.98	0.99	0.89	0.82	0.90	1.00	0.99	0.93	0.80	0.96	0.95	0.87	0.95	0.93
15	MAD	0.18	0.41	0.24	0.23	0.55	0.05	0.41	0.20	0.36	0.26	0.04	0.02	0.07	0.19	0.17	0.47	0.18	0.19	0.20	0.25
	MSE	0.04	0.23	0.08	0.07	0.43	0.00	0.22	0.05	0.17	0.09	0.00	0.00	0.01	0.05	0.04	0.31	0.04	0.05	0.05	0.08
	RMSE	0.20	0.48	0.28	0.27	0.65	0.06	0.47	0.23	0.42	0.30	0.04	0.03	0.07	0.22	0.19	0.55	0.20	0.22	0.23	0.29
	MAPE	8.06	16.26	14.08	10.30	21.03	2.04	18.10	11.32	15.35	12.08	1.83	1.04	3.86	10.07	9.05	16.36	7.74	8.76	9.91	12.44
	I_A	0.82	0.96	0.79	0.79	0.59	0.97	0.96	0.83	0.69	0.74	0.99	1.00	0.96	0.83	0.89	0.53	0.99	0.83	0.82	0.75
25	MAD	0.21	0.48	0.26	0.38	0.40	0.07	0.10	0.62	0.26	0.45	0.18	0.07	0.12	0.19	0.31	0.86	0.31	0.52	0.34	0.04
	MSE	0.06	0.32	0.09	0.19	0.22	0.01	0.01	0.54	0.09	0.28	0.04	0.01	0.02	0.04	0.13	1.01	0.12	0.38	0.16	0.00
	RMSE	0.24	0.56	0.30	0.44	0.47	0.07	0.10	0.73	0.30	0.53	0.20	0.07	0.13	0.21	0.36	1.00	0.34	0.61	0.40	0.04
	MAPE	8.70	16.72	14.06	14.24	14.91	1.97	3.37	33.87	10.92	18.14	8.04	3.35	5.55	9.07	14.57	19.79	7.98	20.98	16.73	1.81

	I_A	0.77	0.96	0.86	0.68	0.67	0.96	1.00	0.65	0.77	0.64	0.83	1.00	0.98	0.84	0.73	0.25	0.99	0.87	0.71	0.99
35	MAD	0.33	1.19	0.83	0.09	0.27	0.19	0.78	0.41	0.09	0.45	0.27	0.16	0.08	0.17	0.41	0.22	2.08	1.23	2.22	1.14
	MSE	0.13	2.02	0.98	0.01	0.10	0.04	0.83	0.23	0.01	0.28	0.10	0.03	0.01	0.04	0.23	0.05	6.14	2.07	7.20	1.86
	RMSE	0.36	1.42	0.99	0.09	0.31	0.19	0.91	0.48	0.09	0.53	0.31	0.17	0.08	0.19	0.48	0.22	2.48	1.44	2.68	1.36
	MAPE	5.46	42.96	34.12	3.18	9.47	3.02	16.85	16.89	3.38	17.41	11.89	6.85	3.22	7.53	16.83	2.26	34.30	20.03	94.45	48.00
	I_A	0.69	0.80	0.50	0.95	0.76	0.88	0.98	0.67	0.95	0.64	0.75	0.99	0.96	0.85	0.66	0.87	0.89	0.43	0.33	0.43
		Sodium adsorption ratio (mol$^{0.5}$ L$^{-1.5}$) of observed and HYDRUS predicted																			
5	MAD	0.15	0.15	0.74	0.36	0.17	0.68	1.24	0.43	0.17	0.32	0.36	0.78	0.63	0.58	0.43	0.76	0.65	1.96	3.00	3.73
	MSE	0.03	0.03	0.66	0.13	0.03	0.61	2.09	0.21	0.03	0.11	0.14	0.78	0.48	0.39	0.19	0.74	0.50	5.31	12.66	19.80
	RMSE	0.18	0.17	0.82	0.36	0.19	0.78	1.45	0.46	0.18	0.32	0.37	0.88	0.69	0.63	0.44	0.86	0.71	2.30	3.56	4.45
	MAPE	1.3	1.3	7.0	3.3	1.5	11.0	14.5	5.1	1.9	3.4	4.6	8.7	6.8	5.4	3.7	9.1	6.5	16.9	22.2	24.6
	I_A	0.93	1.00	0.58	0.86	0.94	0.58	0.97	0.72	0.94	0.88	0.82	0.99	0.60	0.70	0.78	0.54	1.00	0.33	0.35	0.32
15	MAD	0.22	0.85	3.23	0.20	0.11	0.31	0.76	0.41	0.79	0.37	0.11	0.27	0.11	1.20	0.81	1.26	1.17	0.94	1.00	1.97
	MSE	0.05	0.87	14.68	0.04	0.02	0.11	0.76	0.20	0.81	0.15	0.01	0.07	0.01	1.94	0.82	2.14	1.82	1.15	1.28	5.38
	RMSE	0.22	0.93	3.83	0.20	0.15	0.33	0.87	0.45	0.90	0.39	0.11	0.27	0.12	1.39	0.91	1.46	1.35	1.07	1.13	2.32
	MAPE	2.12	6.86	22.36	1.98	1.05	4.60	11.83	6.85	10.99	4.88	1.88	3.58	1.63	13.49	8.60	14.82	14.27	11.32	9.93	18.54
	I_A	0.91	1.00	0.34	0.93	1.00	0.81	0.98	0.79	0.62	0.81	0.97	1.00	0.97	0.52	0.62	0.41	0.97	0.60	0.57	0.42
25	MAD	0.20	1.34	2.62	0.76	0.47	0.17	0.36	0.55	0.19	0.41	0.07	0.13	0.89	0.18	0.29	0.60	3.29	2.96	2.21	1.28
	MSE	0.0	2.3	9.4	0.7	0.2	0.0	0.2	0.4	0.0	0.2	0.0	0.0	1.1	0.0	0.1	0.4	15.5	12.5	6.9	2.2
	RMSE	0.22	1.51	3.07	0.83	0.49	0.17	0.39	0.63	0.20	0.45	0.10	0.13	1.03	0.18	0.30	0.66	3.94	3.53	2.62	1.48
	MAPE	1.6	9.3	16.4	5.9	3.8	2.9	6.4	10.7	3.2	6.4	1.0	1.9	16.1	2.8	4.0	7.9	48.2	41.7	28.0	14.7
	I_A	0.91	0.99	0.26	0.63	0.76	0.94	1.00	0.73	0.92	0.79	0.97	1.00	0.61	0.93	0.86	0.65	0.86	0.36	0.41	0.52
35	MAD	0.25	1.46	2.23	0.22	0.81	0.09	0.32	0.50	0.50	0.24	0.10	0.42	0.80	1.05	0.54	0.44	3.35	3.39	2.99	2.68
	MSE	0.07	2.75	6.75	0.05	0.79	0.01	0.12	0.31	0.32	0.06	0.01	0.21	0.84	1.50	0.37	0.23	16.16	16.58	12.80	10.19
	RMSE	0.26	1.66	2.60	0.23	0.89	0.12	0.34	0.56	0.57	0.25	0.11	0.46	0.92	1.23	0.61	0.48	4.02	4.07	3.58	3.19
	MAPE	1.8	9.8	14.2	1.9	6.4	1.2	5.0	9.3	9.4	4.3	1.4	6.5	13.4	19.2	9.2	6.2	55.9	55.4	43.2	36.0
	I_A	0.90	0.99	0.39	0.92	0.61	0.97	1.00	0.75	0.75	0.90	0.97	1.00	0.64	0.57	0.73	0.75	0.86	0.34	0.36	0.38

Table D.7 Statistical analysis of solution pH, alkalinity (HCO_3^-) extracted at different depths for Soil 3 (Eldorado soil) columns and HYDRUS modelled results for 0, 98, 311, and 650 mg L^{-1} of HCO_3^- irrigation waters.

Soil depth (cm)		***Solution pH of observed and HYDRUS predicted***																			
		Solution HCO_3^-= 0 (mg L^{-1})					***Solution HCO_3^-= 100 (mg L^{-1})***					***Solution HCO_3^-= 310 (mg L^{-1})***					***Solution HCO_3^-= 650 (mg L^{-1})***				
			days																		
		0	**80**	**143**	**214**	**290**	**0**	**80**	**143**	**214**	**290**	**0**	**80**	**143**	**214**	**290**	**0**	**80**	**143**	**214**	**290**
5	MAD	0.65	0.52	0.36	0.51	0.45	0.08	0.27	0.24	0.25	0.20	0.07	1.34	1.55	1.76	1.44	0.09	0.98	1.66	1.57	1.32
	MSE	0.52	0.32	0.14	0.30	0.24	0.01	0.08	0.06	0.06	0.04	0.01	2.43	3.27	4.28	2.78	0.02	1.22	3.77	3.36	2.34
	RMSE	0.72	0.57	0.37	0.55	0.49	0.12	0.28	0.25	0.25	0.20	0.12	1.56	1.81	2.07	1.67	0.13	1.11	1.94	1.83	1.53
	MAPE	8.74	6.70	4.36	6.45	5.78	0.94	3.31	3.00	3.02	2.51	0.86	15.88	18.68	22.01	16.86	1.05	11.08	19.55	18.97	14.79
	I_A	0.43	1.00	0.70	0.65	0.68	0.92	1.00	0.73	0.81	0.85	0.92	0.98	0.13	0.37	0.40	0.91	0.99	0.12	0.39	0.42
15	MAD	0.09	0.47	0.33	0.28	0.30	0.07	0.32	0.45	0.29	0.34	0.07	0.74	1.35	1.61	1.56	0.12	0.16	0.50	0.96	1.43
	MSE	0.01	0.26	0.12	0.08	0.09	0.01	0.11	0.23	0.09	0.12	0.01	0.68	2.44	3.54	3.30	0.02	0.03	0.29	1.20	2.76
	RMSE	0.12	0.51	0.34	0.28	0.30	0.12	0.33	0.48	0.30	0.35	0.12	0.83	1.56	1.88	1.82	0.13	0.17	0.53	1.09	1.66

	MAPE	1.26	5.89	3.89	3.46	3.73	0.88	3.92	5.85	3.76	4.39	0.86	8.91	16.41	19.77	18.80	1.41	1.98	6.01	11.53	17.07
	I_A	0.93	1.00	0.78	0.82	0.85	0.92	1.00	0.69	0.80	0.79	0.92	0.99	0.41	0.38	0.33	0.91	1.00	0.66	0.48	0.26
25	MAD	0.07	0.21	0.12	0.48	0.11	0.07	0.44	0.31	0.44	0.54	0.16	0.32	0.30	1.22	1.41	0.07	0.14	0.30	0.48	0.66
	MSE	0.01	0.04	0.02	0.26	0.02	0.01	0.22	0.10	0.23	0.36	0.03	0.11	0.10	1.99	2.70	0.01	0.02	0.09	0.26	0.54
	RMSE	0.11	0.21	0.14	0.51	0.13	0.12	0.47	0.32	0.48	0.60	0.16	0.33	0.31	1.41	1.64	0.12	0.15	0.31	0.51	0.73
	MAPE	0.91	2.60	1.42	5.81	1.37	0.87	5.56	4.07	5.79	7.00	1.97	3.79	3.71	15.31	17.50	0.84	1.73	3.66	5.85	7.97
	I_A	0.93	1.00	0.93	0.67	0.93	0.93	1.00	0.84	0.64	0.59	0.84	1.00	0.77	0.43	0.40	0.92	1.00	0.74	0.67	0.57
35	MAD	0.36	0.28	0.32	0.20	0.55	0.07	1.07	1.21	1.26	1.29	0.07	0.13	0.20	0.16	0.96	0.09	0.36	0.36	0.30	0.19
	MSE	0.15	0.08	0.11	0.04	0.36	0.01	1.52	1.94	2.12	2.24	0.01	0.02	0.04	0.03	1.20	0.01	0.15	0.14	0.10	0.04
	RMSE	0.38	0.28	0.33	0.20	0.60	0.12	1.23	1.39	1.46	1.50	0.12	0.14	0.20	0.17	1.10	0.12	0.38	0.38	0.31	0.19
	MAPE	4.78	3.47	3.81	2.51	6.67	0.85	13.29	15.25	16.08	16.58	0.87	1.66	2.54	2.02	11.92	1.13	4.50	4.44	3.70	2.37
	I_A	0.66	1.00	0.79	0.85	0.63	0.94	0.98	0.43	0.42	0.42	0.94	1.00	0.85	0.91	0.48	0.94	1.00	0.69	0.75	0.86
		Solution alkalinity (HCO_3^-) of observed and HYDRUS predicted																			
5	MAD	0.22	1.39	0.25	0.67	0.20	0.02	0.52	0.34	0.11	0.09	0.03	1.62	1.69	1.75	1.72	0.06	2.98	4.15	5.43	5.66
	MSE	0.07	2.82	0.09	0.65	0.05	0.00	0.40	0.16	0.02	0.01	0.00	3.79	4.10	4.45	4.29	0.01	12.78	24.94	42.94	46.74
	RMSE	0.26	1.68	0.29	0.80	0.23	0.03	0.63	0.40	0.12	0.10	0.04	1.95	2.03	2.11	2.07	0.09	3.58	4.99	6.55	6.84
	MAPE	31.73	177.32	18.97	39.73	12.72	1.35	60.93	30.08	7.65	6.29	0.96	62.75	62.06	66.43	64.04	0.90	53.87	68.67	101.45	103.87
	I_A	0.75	0.63	0.72	0.54	0.83	0.99	0.89	0.60	0.92	0.94	0.98	0.86	0.08	0.36	0.36	0.95	0.92	0.14	0.25	0.25
15	MAD	0.71	0.09	0.28	0.65	0.40	0.02	0.08	0.33	0.49	0.52	0.03	1.04	1.41	1.45	1.14	0.06	0.65	0.68	1.56	2.97
	MSE	0.73	0.01	0.10	0.59	0.21	0.00	0.01	0.15	0.34	0.38	0.00	1.55	2.85	3.02	1.83	0.01	0.55	0.60	3.37	12.57
	RMSE	0.85	0.09	0.31	0.77	0.45	0.02	0.08	0.38	0.58	0.62	0.04	1.24	1.69	1.74	1.35	0.09	0.74	0.78	1.84	3.55
	MAPE	65.33	3.51	7.29	17.74	11.04	0.90	4.52	15.94	21.51	22.39	0.88	52.71	55.96	48.83	32.15	0.91	11.80	11.16	23.73	44.59
	I_A	0.29	1.00	0.75	0.54	0.99	0.99	1.00	0.71	0.61	0.74	0.98	0.94	0.39	0.39	0.77	0.95	0.99	0.56	0.38	0.39
25	MAD	0.33	0.83	1.17	0.30	0.06	0.04	0.81	1.20	1.35	1.29	0.04	0.63	0.70	0.11	0.47	0.07	0.25	0.25	0.65	0.33
	MSE	0.15	0.97	1.93	0.11	0.01	0.00	0.94	2.08	2.64	2.41	0.00	0.54	0.66	0.01	0.28	0.01	0.07	0.07	0.54	0.12
	RMSE	0.38	0.99	1.39	0.33	0.07	0.04	0.97	1.44	1.63	1.55	0.05	0.74	0.82	0.11	0.53	0.09	0.26	0.26	0.73	0.35
	MAPE	12.64	20.52	21.32	6.93	1.43	2.10	28.81	36.08	38.75	36.41	1.21	16.28	16.33	2.50	10.63	1.24	4.35	3.88	8.99	4.49
	I_A	0.64	0.95	0.53	0.74	0.97	0.99	0.91	0.38	0.39	0.40	0.98	0.97	0.87	0.94	0.65	0.95	1.00	0.82	0.54	0.71
35	MAD	0.34	0.87	1.60	0.55	0.90	0.02	0.25	0.93	2.02	2.13	0.05	0.74	1.52	1.75	1.22	0.05	0.77	1.60	1.49	1.50
	MSE	0.15	1.06	3.67	0.39	1.11	0.00	0.08	1.23	5.95	6.61	0.00	0.76	3.33	4.40	2.08	0.01	0.78	3.58	3.08	3.13
	RMSE	0.39	1.03	1.92	0.62	1.05	0.03	0.28	1.11	2.44	2.57	0.05	0.87	1.83	2.10	1.44	0.09	0.89	1.89	1.76	1.77
	MAPE	11.35	19.70	27.47	10.85	17.23	0.88	8.09	23.26	36.58	37.84	1.48	17.61	28.89	30.08	20.57	0.88	10.91	19.41	18.37	18.19
	I_A	0.68	0.95	0.36	0.59	0.47	0.99	0.99	0.46	0.33	0.32	0.98	0.96	0.37	0.35	0.41	0.96	0.99	0.36	0.37	0.37

Appendix E. Hydraulic conductivity reduction code in HYDRUS model

E.1. New generalised function code

The following code can be used to if the new generalised K_s reduction function due to pH developed in this research project is used to predict K_s reduction in HYDRUS model. The following code was updated from previous code for K_s reduction due to salinity, sodicity and pH of soil solution.

```
if(lKRed) then
ssConc=Conc(1,i)+Conc(2,i)+Conc(3,i)+Conc(4,i)
ESP=0.
if(ChPar(4,M).gt.0.) ESP=XConc(3,i)/ChPar(4,M)*100.
Clay=.1
ESP1=1.24
ESP2=11.63
if(ESP.le.25.) then
c=35.
an=1.
else if(ESP.gt.25..and.ESP.lt.50.) then
c=932.
an=2.
else if(ESP.ge.50.) then
c=25000.
an=3.
end if
AESP=amax1(ESP-(ESP1+ESP2*alog10(ssConc)),0.01)
d=0.
if(ssConc.lt.300.) d=356.4*ssConc**(-0.5)+1.2
if(ssConc.eq.0.) d=1.e10
if(lYounes) then
Clay=RedKPar(4)
ESP1=RedKPar(8)
ESP2=RedKPar(9)
ESP3=RedKPar(10)
c    ESP4=RedKPar(11)
an=RedKPar(5)
if(ESP.le.ESP3) then
g1=RedKPar(1)
xm1=RedKPar(2)
c=g1*exp(xm1*(ESP/100.))
end if
c   if(ESP.le.ESP3) then
c   c=RedKPar(1)
c   an=RedKPar(5)
c   else if(ESP.gt.ESP3.and.ESP.lt.ESP4) then
c   c=RedKPar(2)
c   an=RedKPar(6)
c   else if(ESP.ge.ESP3) then
c   c=RedKPar(3)
c   an=RedKPar(7)
c   end if
AESP=amax1(ESP-(ESP1+ESP2*alog(ssConc)),0.01)
d=0.
```

```
if(ssConc.lt.300.) d=356.4*ssConc**(-0.5)-20.5767
if(ssConc.eq.0.) d=1.e10
end if
xx=Clay*3.6e-4*AESP*d
xpH=1.
if(pH.gt.7.2) xpH=2.242-0.172*pH
if(pH.gt.9.5) xpH=0.6
red(i)=amax1((1.-c*xx**an/(1.+c*xx**an))*xpH,0.00001)
red(i)=amin1(1.,red(i))
if(red(i).lt.xRed) xRed=red(i)      ! Only for print
end if
```

E.2. A pedotransfer function code for *K*$_s$ reduction due to pH

The *K*$_s$ reduction code was also updated to incorporate pedotransfer function developed in this study into HYDRUS model for predicting *K*$_s$ reduction due to pH. The following code provides the *K*$_s$ reduction due to salinity, sodicity and pH of soil solution using nonlinear (pedotransfer) function for pH of applied solution.

```
if(lKRed) then
ssConc=Conc(1,i)+Conc(2,i)+Conc(3,i)+Conc(4,i)
ESP=0.
if(ChPar(4,M).gt.0.) ESP=XConc(3,i)/ChPar(4,M)*100.
Clay=.1
ESP1=1.24
ESP2=11.63
if(ESP.le.25.) then
c=35.
an=1.
else if(ESP.gt.25..and.ESP.lt.50.) then
c=932.
an=2.
else if(ESP.ge.50.) then
c=25000.
an=3.
end if
AESP=amax1(ESP-(ESP1+ESP2*alog10(ssConc)),0.01)
d=0.
if(ssConc.lt.300.) d=356.4*ssConc**(-0.5)+1.2
if(ssConc.eq.0.) d=1.e10
if(lYounes) then
Clay=RedKPar(4)
ESP1=RedKPar(8)
ESP2=RedKPar(9)
```

```
ESP3=RedKPar(10)
c    ESP4=RedKPar(11)
an=RedKPar(5)
if(ESP.le.ESP3) then
g1=RedKPar(1)
xm1=RedKPar(2)
c=g1*exp(xm1*(ESP/100.))
end if
c   if(ESP.le.ESP3) then
c   c=RedKPar(1)
c   an=RedKPar(5)
c   else if(ESP.gt.ESP3.and.ESP.lt.ESP4) then
c   c=RedKPar(2)
c   an=RedKPar(6)
c   else if(ESP.ge.ESP3) then
c   c=RedKPar(3)
c   an=RedKPar(7)
c   end if
AESP=amax1(ESP-(ESP1+ESP2*alog(ssConc)),0.01)
d=0.
if(ssConc.lt.300.) d=356.4*ssConc**(-0.5)-20.5767
if(ssConc.eq.0.) d=1.e10
end if
xx=Clay*3.6e-4*AESP*d
xpH= (1.25-pH*log(ssConc)/21.72-7.42*pH+28.8*log(ssConc)+0.33*Clay)
xpH=amin1(1.,xpH)
red(i)=amax1((1.-c*xx**an/(1.+c*xx**an))*xpH,0.00001)
red(i)=amin1(1.,red(i))
if(red(i).lt.xRed) xRed=red(i)    ! Only for print
end if
```

Appendix F. Threshold electrolyte concentration model surface fitting residual errors

The residual errors associated with the disaggregation model surface fitting for normal threshold electrolyte concentration (C_{TH}) and C_{TH} of solutions treated with different levels of alkaline anion (HCO_3^-). The residual errors of C_{TH} for Wariven soil, Eldorado soil, Dalby soil and Maryborough soil are showed in Figure F.1, F.2, F.3 and F.4, respectively.

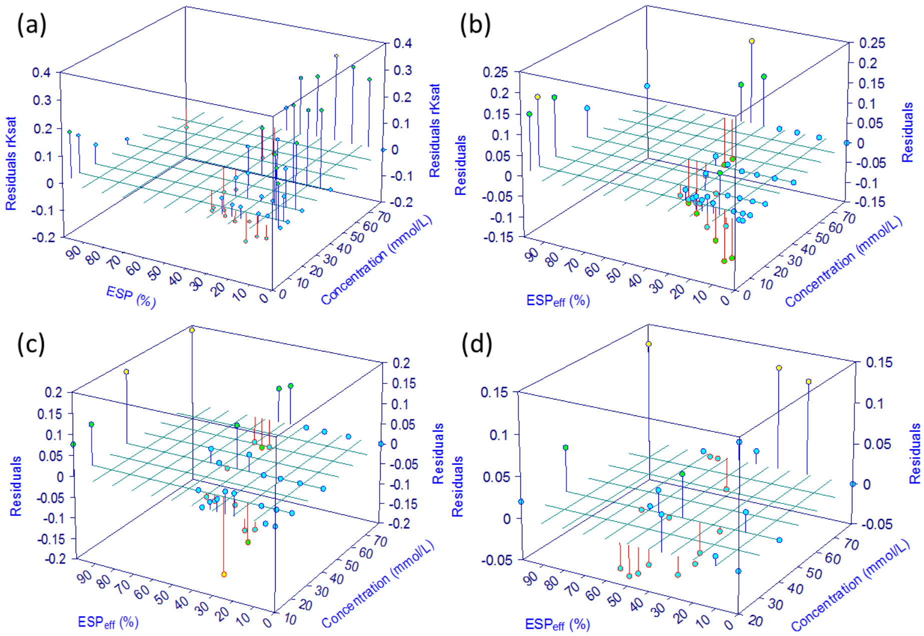

Figure F.1 Residual errors of reduction in saturated hydraulic conductivity (r_{Ks}) for Soil 1 (Wariven soil) treated with alkalinity at a) 0 mg L^{-1}, b) 100 mg L^{-1}, c) 400 mg L^{-1} and d) 1000 mg L^{-1}. The 3-Dimensional surfaces and model parameters and associated statistics are presented in Chapter 7.

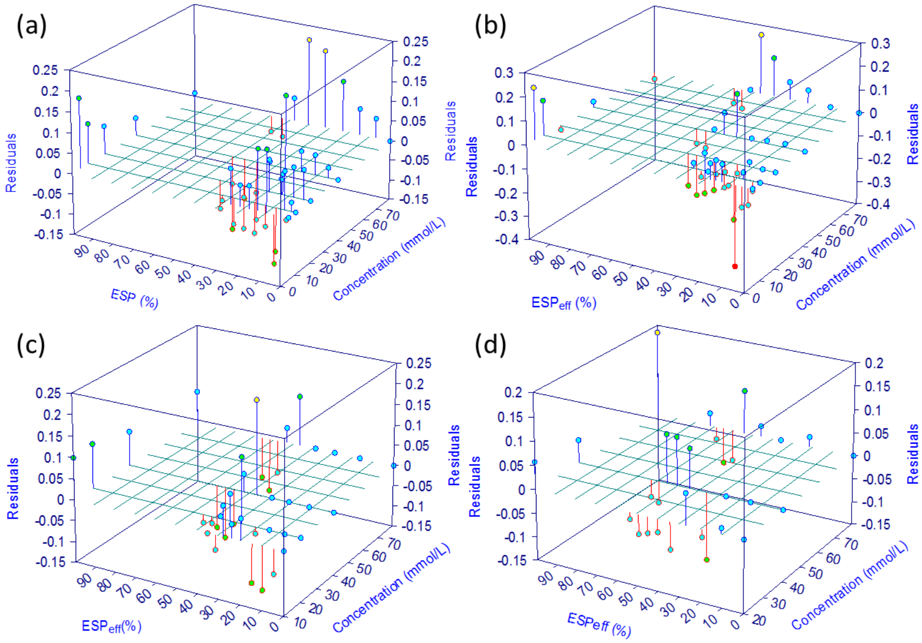

Figure F.2 Residual errors of reduction in saturated hydraulic conductivity (r_{Ks}) for Soil 2 (Eldorado soil) treated with alkalinity at a) 0 mg L^{-1}, b) 100 mg L^{-1}, c) 400 mg L^{-1} and d) 1000 mg L^{-1}. The 3-Dimensional surfaces and model parameters and associated statistics are presented in Chapter 7.

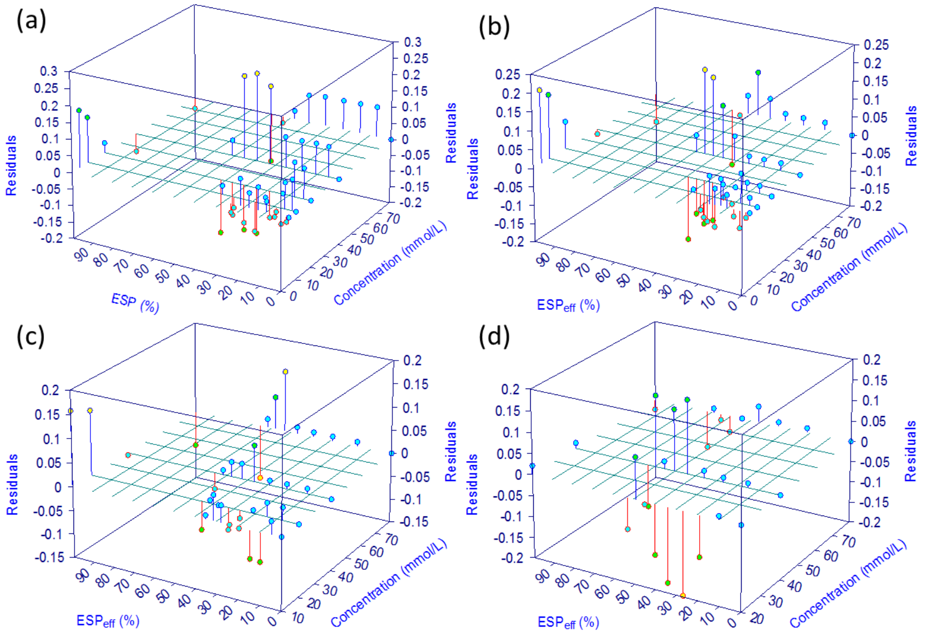

Figure F.3 Residual errors of reduction in saturated hydraulic conductivity (r_{Ks}) for Soil 3 (Dalby soil) treated with alkalinity at a) 0 mg L^{-1}, b) 100 mg L^{-1}, c) 400 mg L^{-1} and d) 1000 mg L^{-1}. The 3-Dimensional surfaces and model parameters and associated statistics are presented in Chapter 7.

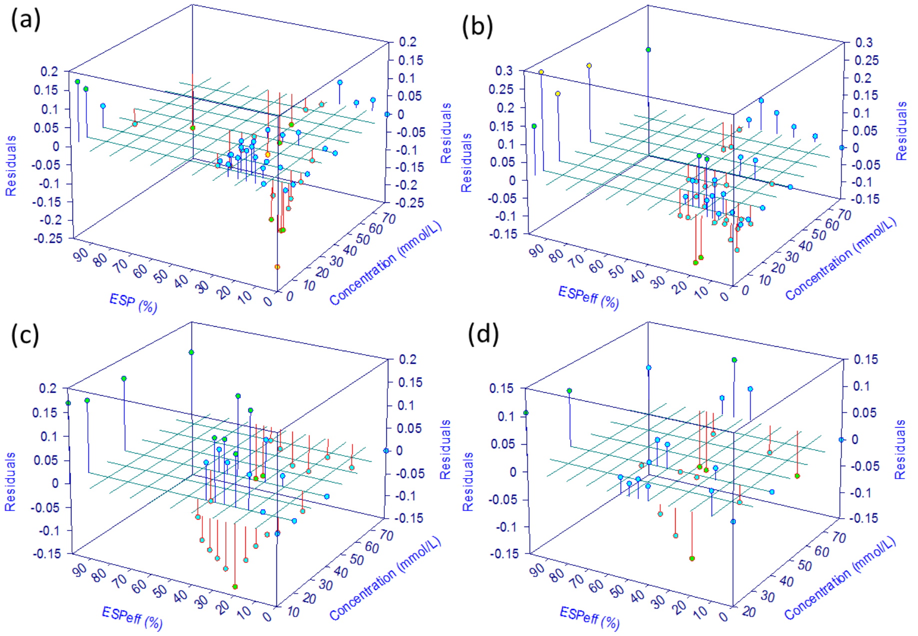

Figure F.4 Residual errors of reduction in saturated hydraulic conductivity (r_{Ks}) for Soil 4 (Maryborough soil) treated with alkalinity at a) 0 mg L^{-1}, b) 100 mg L^{-1}, c) 400 mg L^{-1} and d) 1000 mg L^{-1}. The 3-Dimensional surfaces and model parameters and associated statistics are presented in Chapter 7.

Appendix G. Land amendment plan

Initial land amendment trials plan for two soils in New South Wales, Australia

G.1. Wariven site

SOIL AMENDMENT TRIAL

Wariven East Pivot (Northern ½) – see map on Figure G.1.

TREATMENTS:

- Gypsum @ 4 Ton ha^{-1} plus Lime @ 2 Ton ha^{-1}
- Gypsum @ 4 Ton ha^{-1}plus Lime @ 2 Ton ha^{-1} plus Sulfur @ 200 kg ha^{-1}
- Sulfur @ 200kg ha^{-1}
- Sulfur @ 100 kg ha^{-1} (remainder of field)
- Nil

Treatments applied 6 April 2016 with spreader followed by Agro-Plough.

Figure G.1 Land amendment of the selected area of Wariven site.

Table G.1 Land amendment field plan for Wariven soil

Remainder of field	Plot 1 36m	Plot 2 36m	Plot 3 36m	Plot 4 36m	Plot 5 36m	Plot 6 36m	Plot 7 36m	Plot 8 36m	Remainder of field
Sulfur @ 100kg/ha	G @ 4t L @ 2t	G @ 4t L @ 2t S @ 200kg	S @ 200kg	NIL	G @ 4t L @ 2t S @ 200kg	G @ 4t L @ 2t	NIL	S @ 200kg	S @ 100kg/ha
FLAG COLOURS	Pink	Pink blue	blue	nil	Pink blue	pink	nil	blue	

←NORTH 78m to Pivot entrance road →

NOTES:

- Plots are 36 m wide but all assessments should be done in the center 12m to account for spreading variability.

G.2. Eldorado site

SOIL AMENDMENT TRIAL

Eldorado East Pivot (Northern ½) – see map on Figure G.2

TREATMENTS applied by spreader Wednesday 10 August 2016:

- Gypsum @ 2 Ton ha^{-1}
- Gypsum @ 2 Ton ha^{-1} plus Sulfur @ 220 kg ha^{-1}
- Sulfur @ 220 kg ha^{-1}
- Nil

Figure G.2 Land amendment of the selected area of Eldorado site

Table G.2 Land amendment field plan for Eldorado soil

12m buffer to center road Gypsum @ 2t/ha	Plot 1 24m	Plot 2 24m	Plot 3 24m	Plot 4 24m	Plot 5 24m	Plot 6 24m	Plot 7 24m	Plot 8 24m	Plot 9 24m	Plot 10 24m	Plot 11 24m	Plot 12 Remainder of field
	G@ 2t/ha	S@ 220kg	G @ 2t S @ 220kg	NIL	S @ 220kg	NIL	G @ 2t S @ 220kg	G @ 2t/ha	NIL	S @ 220kg	G @ 2t S @ 220kg	G @ 2t/ha
	Rep 1				Rep 2				Rep 3			

NORTH ➔

NOTES:

- Plots are 24m wide but all assessments should be done in the center to account for spreading variability.
- Plots are marked with small wire pegs with labelled flags on them. Flags are on the left hand side of each plot (southern side). Tall plastic pegs mark the start and end of the trial.
- Average run length 920m (780-960m) – 2.2ha per plot. Total trial = 26.4ha – 288m wide
- Approximate product quantities required
    - 2.7T Sulfur
    - 27T Gypsum