MAGNESIC SOILS: FIRST PRINCIPLE SOIL MANAGEMENT STRATEGIES FOR INCREASED PRODUCTIVITY

A Thesis submitted by

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Abstract

Irrigation waters containing considerable amounts of magnesium (Mg) are increasingly used in farming, due to the scarcity of good quality irrigation water. This increases the concern for Mg accumulating in soil systems. Together with naturally formed magnesic soils, irrigation induced Mg affected soils have been reported in many countries. In magnesic soils – for which there is limited information – the combination of poor soil structural properties, calcium deficiency and magnesium toxicity have been suggested as stress factors for plants. Unfortunately, there is a paucity of conclusive information detailing Mg effects on soil structure, with existing literature suggesting Mg has a specific effect. This thesis is focused on the effect of Mg, either Mg in irrigation water or soils, on the soil structural stability. This is one of the prerequisites in decision making for soil management that maintains and/or increases soil productivity.

To investigate the effect of Mg on soil structural stability, fundamental studies based in the laboratory were conducted in both soil clay suspensions and aggregated systems. Other factors influencing structural stability were also considered, including soil pH, electrolyte concentration, clay mineralogy, organic matter, texture and mechanical stress. To quantify clay dispersion, a rapid and inexpensive method was developed via use of a turbidimeter. The measured turbidity (NTU) of dispersed clay in suspension, can be easily and quantitatively converted to the dispersed clay quantity (mg/L, % of soil). This method was used in all experimentations throughout the whole thesis for the investigation of the effect of Mg on soil structural stability.

The dispersive behaviour of Mg-saturated soil clay with contrasting mineralogy was studied at pH 3–8. The results demonstrated that, at low pH, Mg clays flocculate, although different clay types had different flocculation ranges; at neutral pH, Mg clays had higher dispersed clay (%) than Ca clays under similar conditions. This study further showed that Mg clays have greater net negative charge (more negative zeta potential value) and smaller mean particle size than Ca clays at similar conditions. Nevertheless, zeta potential for Mg and Ca clays are >-30 mV, suggesting Mg has a flocculative effect, rather than a dispersive effect, on the soil-clay suspensions, whereby these are the same forces that would enact within an aggregated system; *i.e.* irrespective of Mg concentrations within the pH range of this study, the zeta potential results indicate that an aggregated system would be expected.

Permeability is one of the most important indicators of soil structural stability. In exploring the effect of Mg on saturated hydraulic conductivity (K_{sat}), four contrasting soils were leached with a range of concentrations of Mg solutions. When the electrolyte concentration of leaching solution was below the critical flocculation concentration (CFC) of the soil clays, the K_{sat} of all soils reduced rapidly. However, the extremely low turbidity (<15 NTU) of leachate indicated Mg caused negligible clay dispersion (<0.016% dispersed clay of soil). There was no visual dispersion occurring in the aggregate stability test on Mg soil aggregates. As compared to Ca, Mg has a disaggregation effect on soil structural stability by reducing K_{sat} and increasing desorption of dissolved organic carbon from the clay surface. The increased disaggregation in Mg systems, due to enhanced inter-crystalline and intra-crystalline swelling, was the identified hydraulic reduction mechanism, meaning clay domains remain non-dispersive.

The Cation ratio of soil structural stability (CROSS) and exchangeable dispersive percentage (EDP) have been recently proposed to replace the traditional sodium absorption ratio (SAR) and exchangeable sodium percentage (ESP) for predicting soil structural stability. CROSS and EDP have incorporated the dispersive coefficients a[K]=0.556 and c[Mg]=0.037 and flocculative coefficient b[Mg]=0.60, transforming dispersive effect of K and Mg to equivalent Na as well as the flocculative effect of Mg to equivalent Ca. However, these coefficients, a[K]=0.556, b[Mg]=0.60 and c[Mg]=0.037, in the generalised CROSS and EDP are derived from the flocculating power of Na, K, Mg and Ca based on a limited number of soil clays. To further explore the effect of Mg on different soil types and re-examine the coefficients a[K], b[Mg] and c[Mg], the CFC of seventeen contrasting soils were studied. Significant differences ($P<0.05$) in the CFC values were found for the same homoionic clay system, *i.e.* Na, K, Mg and Ca. The dispersive coefficients of a[K] and c[Mg] and flocculative coefficient of b[Mg] were calculated for each soil. These derived coefficients were further used in calculating specific CROSS and specific EDP. Through a sensitivity simulation, both the variation in the coefficient a[K] and b[Mg] for studied soils were found to significantly affect the absolute error between specific and generalised CROSS. In regards to EDP, the dispersive coefficient a[K] proved to be playing the primary role in determining the difference between the specific and generalised EDP, while the dispersive coefficient c[Mg] had negligible impact in predicting soil structural stability. The work recommended the removal of the Mg term from the EDP, and reinforced that the soil-specific coefficients should be used in the determination of soil structural relations.

The different effects between Mg and Ca on soil dispersive behaviour are due to their inherent difference. Despite both Ca and Mg being divalent valence, the covalency degree of Ca-clay bond was stronger than that of Mg-clay, in all circumstances, as indicated by ionicity indices. This mechanism was confirmed by the higher dispersed clay (%), more negative zeta potentials, and smaller particle size of Mg clays. Consequently, the ionicity index, which describes the ionicity (and covalency) degree of the clay–cation bond, together with solution pH, electrical conductivity, zeta potential and particle size has been used to generate a model to predict the dispersive behaviour of clay suspensions. This pedotransfer function is promising, but requires more work for general use and should be the focus of future investigations in this field of study.

Certification of Thesis

This Thesis is the work of Yingcan Zhu except where otherwise acknowledged, with the majority of the authorship of the papers presented as a Thesis by Publication undertaken by the student. The work is original and has not previously been submitted for any other award, except where acknowledged.

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Student and supervisors signatures of endorsement are held at the University of Southern Queensland.

Statement of Contribution

Throughout the course of this candidature the four experimental chapters have been published or submitted to peer reviewed journals, as indicated below.

<u>Chapter 3</u>

Zhu, Y.*, Marchuk, A., Bennett, J.M., 2016. Rapid method for assessment of soil structural stability by turbidimeter. *Soil Science Society of America Journal* 80(6), 1629-1637.

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Contributor	Statement of contribution
Author 1 Mrs Yingcan Zhu (Candidate)	Conception and design (50%) Analysis and interpretation (50%) Drafting and production (60%)
Author 2 Dr Alla Marchuk	Conception and design (25%) Analysis and interpretation (25%) Drafting and production (20%)
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<u>Chapter 4</u>

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Chapter 5

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Chapter 6

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Abbreviations and acronyms used

AFM	Atomic force microscopy
C_{TH}	Threshold electrolyte concentration (TEC)
C_{TU}	Threshold turbidity concentration
CEC	Cation exchange capacity
CFC	Critical flocculation concentration
CI	Covalency index
CROSS	Cation ratio of soil structural stability
DI	Deionised water
DDL	Diffuse double layer
DLVO	Derjaguin, Landau, Verwey and Overbeek theory
EAED	Electron-acceptor and electron-donor
ESP	Exchangeable sodium percentage
ECR	Exchangeable cation ratio
EDP	Exchangeable dispersion percentage
EMP	Exchangeable magnesium percentage
EPP	Exchangeable potassium percentage
ICP- MS	Inductive coupled plasma atomic mass
II	Ionicity index
K	Soil permeability
K_{sat}	Saturated hydraulic conductivity
PB	Poisson-Boltzmann
PZC	Point of zero charge
PAR	Potassium absorption ratio
SAR	Sodium adsorption ratio
SFA	Surface force apparatus
TCC	Total cation concentration

Chemicals and minerals

$CaSO_4 \cdot 2H_2O$	Calcium sulphate (gypsum)
$Al_5MgSi_{12}O_{30}(OH)_6$	Montmorillonite
$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	Illite
$Mg_3Si_4O_{10}(OH)_{2.2}H_2O$	Vermiculite
$Al_2Mg_5Si_3O_{10}(OH)_8$	Chlorite
$CaCl_2$	Calcium chloride
$Ca(OH)_2$	Calcium hydroxide
$CaCO_3 \cdot MgCO_3$	Dolomite
$H_4Mg_3Si_2O_9$	Serpentine
$NaCl$	Sodium chloride
$NaOH$	Sodium hydroxide
$Na_2C_2O_4$	Sodium oxalate
KCl	Potassium chloride
KOH	Potassium hydroxide
$MgCl_2$	Magnesium chloride
$Mg(OH)_2$	Magnesium hydroxide (brucite)
$MgSO_4$	Magnesium sulphate
$MgCO_3$	Magnesium carbonate

1. Introduction: General background, aims and thesis overview

1.1. Background

Worldwide there are approximately 950 million ha of land estimated to be salt-affected, with salinity affecting 23% of arable land, and saline-sodic soils affecting a further 10% (Szabolcs, 1989). In Australia, the annual loss of potential production, due to sodicity, is approximately AUD$1035 million (Hajkowicz and Young, 2005). A great body of literature on soil structural stability has focused on the deleterious effects of soluble and exchangeable sodium. On this basis, industry and the scientific community have historically accepted sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP) as the standard indices for the prediction of soil structural deterioration (Sumner, 1993; US Salinity Laboratory Staff, 1954).

Magnesic soils (soils with appreciable, usually dominant, Mg concentration) are considered as salt-affected soils. While they are generally widely distributed (depending on the definition used), magnesic soils have been afforded less attention, relative to saline and sodic soils, in terms of soil structural stability. In Australia, a number of soils contain high proportions of exchangeable Mg, particularly in the subsoil (Qadir and Schubert, 2002; Tucker, 1983). It has been reported that 7% of Sodosol soils have Ca/Mg ratios less than 0.1 in the major part of the B2 horizon (Isbell, 1997; 2016), where Sodosol soils account for 13.0% of Australian soils. In addition, wastewaters containing appreciable quantities of Mg are increasingly used in farming, due to the scarcity of high quality fresh water (Skilton et al., 2000; Vyshpolsky et al., 2008). Consequently, the effect of Mg in either the soil solution, or on the exchange complex, is suggested to play a critical role in structural stability. However, to date, only very limited studies have reported on the effect of Mg on soil clay dispersion and its structural stability. The results of these studies suggest that Mg effects vary from positive to negative (Curtin et al., 1994b; Dontsova and Norton, 1999; Emerson and Chi, 1977; Keren, 1991; Rengasamy et al., 1986; US Salinity Laboratory Staff, 1954). This has led to the Mg effect on soil structure being described as a specific one. As compared to Ca and Na, there remains a paucity of information explaining why the effect of Mg is specific, and what mechanism/s describe its influence on soil structural stability.

The reasons for this apparent research gap, concerning the effect of Mg on soil structural stability, seem to be historical. Since 1954, Mg and Ca have been grouped together as having similar beneficial effects on structural stability by the US Salinity Laboratory Staff (1954). On this basis, neither the diagnostics, nor the distribution of magnesic soils, have been sufficiently elaborated on (Szabolcs, 1989). Subsequently, the surge of soil structural research in the 1970s through 1980s (Sumner, 1993) only commenced to identify magnesic soils as important to soil structure at this point (Rengasamy, 1983), while the effects of Na, and monovalent ions in general, had been recognised prior to the early 1900s (Quirk and Schofield, 1955). Moreover, magnesic soils have often been studied in combination with sodic soils, alkali soils or saline soils. Consequently, the structural stability of magnesic soils as well as the effects of magnesium on soil structural stability are not as well understood. However, there is a current requirement for comprehensive research on Mg effects on soil structural stability in order that it be included within the dynamics of soil hydraulic models and pedotransfer functions.

In brief, soil structural stability refers to the ability of soil aggregates and their arrangement, to retain, or resist, change in pore geometry when exposed to an external force (Amezketa, 1999; Bronick and Lal, 2005; Lal, 1991; Oades, 1984). A favourable soil structure is critical for improving soil fertility, enhancing porosity, decreasing erodibility and increasing productivity (Amezketa, 1999; Bronick and Lal, 2005). In contrast, poor soil structure can often lead to low water infiltration, hard-setting, poor aeration and, consequently, low production (Dexter, 2004). Hence, systematic study of the effect of Mg on soil structural stability, in terms of fundamental approaches, is required for the provision of management advice on the maintenance and/or increased productivity of magnesic soils.

In magnesic soils, Mg is suggested to have a prevailing impact on structural stability (Qadir et al., 2018; Zhang and Norton, 2002). Although Mg was considered equivalent to Ca in having beneficial effects on soil structural stability, negative effects of Mg on hydraulic conductivity and infiltration have been reported (Emerson and Smith, 1970; Qadir et al., 2018; Rahman and Rowell, 1979; Rengasamy et al., 1986; Smith et al., 2015). The direct effect of Mg in decreasing structural stability is termed the ‘specific effect of Mg’ (Curtin et al., 1994b; Rahman and Rowell, 1979). In addition to the specific effect of Mg, a number of other physical and chemical factors also have influence on structural stability, including soil clay content and mineralogy, soil pH, electrolyte concentration, composition of the cations on exchangeable complexes, organic matter, mechanical stress applied to soil and the water content at which disturbance occurs (Bakker et al., 1973; Chi et al., 1977; Curtin et al., 1994a; Frenkel et al., 1978; Goldberg et al., 1988; Nelson et al., 1999; Rengasamy, 1983). For Na and Ca soil and clay systems, pH affects clay dispersion primarily by changing the net negative charge, which also depends on clay mineralogy (Chorom and Rengasamy, 1995; Delgado et al., 1986; Williams and Williams, 1978). However, the effects of clay mineralogy and pH on net negative charge and dispersive behaviour of K and Mg clays have not been fully explored. Further investigation into the role of pH on the net negative charge of K and Mg clays is required, as these factors are likely to partially explain the soil-specific effect.

Recent investigations have demonstrated that water interaction with clays is dictated by the degree of ionicity of clay–cation bonds (Marchuk and Rengasamy, 2011; Marchuk et al., 2013b). As the ionicity indices of the cations decrease (Na>K>Mg>Ca), the degree of covalency in clay–cation bonds increase and clay particles are more aggregated. According to the ionicity concept, the Mg ion has a smaller degree of covalency in bonding with clay than that of Ca and, as a consequence, the Mg clays are less aggregated than Ca clays (Marchuk and Rengasamy, 2011). Similarly, the monovalent cation K has a lower degree of ionicity than Na, and therefore has less effect on clay dispersion. The ionicity index is shown to strongly correlate with turbidity, zeta potential (net negative charge) and mean particle size of clay suspensions (Marchuk and Rengasamy, 2011; Marchuk et al., 2013b). From this point of view, ionicity index should be considered together with pH, EC, net negative charge and mean particle size, for the prediction and understanding of the dynamics of dispersive systems on a soil-specific basis.

Permeability is another important indicator of soil structural stability, which directly influences the movement of water and nutrients, as well as the availability of these to plants, and the holistic function of a soil. Due to the scarcity of good quality irrigation water, wastewater containing appreciable amounts of Mg are used in farming (Karimov et al., 2009; Qadir et al., 2018; Skilton et al., 2000; Vyshpolsky et al., 2008). In general, the deterioration of structure and hydraulic conductivity occurs when the electrolyte concentration of applied solution decreases (Bennett et al., 2019; de Menezes et al., 2014; Ezlit et al., 2013; Jayawardane, 1979; McNeal and Coleman, 1966) and/or monovalent ions increase (Bennett et al., 2016b; Jayawardane et al., 2011; Rengasamy and Marchuk, 2011). Furthermore, dissolved organic matter increases clay dispersion in soils dominant with monovalent ions (Goldberg et al., 1990; Marchuk et al., 2013a). To date, there is only limited research concerning the effect of Mg on soil saturated hydraulic conductivity (K_{sat}) and the interaction between Mg and dissolved organic matter. Further investigation is required to elucidate the extent of the Mg effect on K_{sat} of soils with contrasting clay mineralogy, plus the interaction of Mg with soil organic matter, which are prudent in driving our understanding of soil structural dynamics.

Recently, Rengasamy and Marchuk (2011) proposed a new model of cation ratio of soil structural stability (CROSS) to replace the previous SAR model, where CROSS incorporates the dispersive effects of Na and K and the flocculating effects of Mg and Ca according to their flocculation powers. Later, Bennett et al. (2016a) proposed exchangeable dispersive percentage (EDP) as an alternative index to ESP for explanation of dispersion occurring in soils, which incorporates the dispersive effect of Na and K, as well as the potential Mg dispersive effect with a conditional caveat. The two new indices, CROSS and EDP, were found to correlate with clay dispersion better than SAR and ESP (Bennett et al., 2016a; Rengasamy and Marchuk, 2011). Regarding the EDP conditional caveat for Mg dispersive effect, the incorporation of the Mg dispersive term did not always improve the prediction of soil clay dispersive behaviour (Bennett et al., 2016a; Smith et al., 2015); it was found that unless the Mg dispersive term was >40% effective, as compared to 100% Mg system, then inclusion of Mg worsened the predictive capability. This suggests that Mg has an interacting role with the other cations (Bennett et al., 2016a). Furthermore, as the coefficients in CROSS and EDP – derived from flocculation powers – are verified on a small number of soils, it is unclear how variable the coefficients of equivalence used in CROSS and EDP are. Smith et al. (2015) proposed that these coefficients can be optimized, showing a better correlation with threshold electrolyte concentration (C_{TH}) for the Sodosol soils their work was based upon. From this finding, Smith et al. (2015) and Bennett et al. (2016a) suggested that the coefficients of equivalence for K and Mg in relation to Na, and Mg in relation to Ca, were optimisable on a soil-specific basis. There is, therefore, a need to validate the flocculation power for a wider range of soils with specific properties, as this will be important in describing the dynamic effect of CROSS and EDP within soil hydraulic models.

It is vital to develop a rapid and accurate method for the quantitative determination of clay dispersion. In order to easily evaluate soil structural stability and include such data in future models, cheap and rapid methods are paramount to industry adoption, and to further simplify scientific approaches. Clay dispersion under minimal disturbance and intense external energy input can be analysed by spontaneous and mechanical dispersion tests respectively (Rengasamy et al., 1984). The amount of water dispersible clay from the two tests is usually assessed gravimetrically or via spectrophotometric methods (Amézketa and Aragüés, 1995b; Czyż and Dexter, 2015; Rengasamy et al., 1984; Yousaf et al., 1987a). Compared with the gravimetric approach, turbidimetry is more efficient and requires only a small volume of clay suspension. However, the requirement remains to convert the practically meaningless turbidity unit (NTU) into grams per litre of dispersed clay for better quantification. Such a method would be highly useful in soil stability experimentation in terms of collecting large data sets that will facilitate the development of more complex models.

1.2. Aims and objectives

Given this background discussion, the aim of this research is to investigate and quantify the controlling mechanisms of soil structure in magnesic soils, based on a fundamental study of colloidal interactions between Mg and other major cations; investigating this in a range of soils with different physicochemical properties, through improved dispersion assessment models, which can be further used to guide precise management for increased productivity.

The specific objectives include:

1. Development of a rapid and accurate method for assessment of soil structural stability for different types of soils using turbidimeter,
    a. analyse the relationship between the turbidity unit (NTU) and dispersed clay (g/L, %) and their affecting factors; and,
    b. build a clay dispersion assessment chart and recommendations based on the new indices CROSS and EDP;
2. Investigation of the effect of Mg on clay dispersive behaviour with contrasting soil clay mineralogy at changing pH as compared to Ca clays, further validating the role of ionic bonding on clay behaviour;
3. Identify and quantifying the effect of Mg on soil saturated hydraulic conductivity (K_{sat}) and its interaction with organic matter on contrasting soils, and
4. Further validate the flocculation power of Mg as compared to Ca for a range of diverse soils through critical flocculation concentration study, and relate this to expected influence on predictive indices.

1.3. Thesis overview

This thesis has been prepared in the format of a Thesis by Publication.

In ***Chapter 1***, the issues and general background associated with magnesic soils are introduced, and the key knowledge gaps in the current understanding of effect of Mg in soil structural stability are pointed out. This chapter also identifies and narrows the research topics for the whole project.

Chapter 2 presents a full literature review on the current research into magnesic soils, and highlights the knowledge gaps that require further study. It presents the whole picture of magnesic soils – definition, distribution and formation. The effect of Mg on soil structural stability and plant growth are discussed. Factors, in addition to Mg, that affect structural stability of soils are reviewed and discussed as well. With the comprehensive information and the broad literature data to date, this chapter proposes the justification for completing this research project.

In ***Chapter 3***, a rapid and inexpensive method to evaluate soil structural stability using turbidimeter is proposed and experimentally verified. This work has been published in Soil Science Society of America Journal (Zhu et al., 2016). Initially, this chapter validates the linearity of a turbidity of clay suspension by dilution, and reports a strong correlation between turbidity and dispersed clay (%) for each soil. This work then provides a semi-quantitative dispersion assessment chart, which is intended to provide rapid diagnosis and to act as an important index for soil management practitioners. Strong correlations are presented between each of the two indices, *i.e.* CROSS and EDP, and the dispersed clay with combination of ionic strength and clay content. This new method has been applied through following chapters.

In ***Chapter 4***, the dispersive behaviours of Mg and K clays of different mineralogy are investigated at changing pH, and compared to the behaviours of Ca and Na clays under equivalent conditions, in relation to the ionicity concept. Soil clays, dominated by montmorillonite, illite and kaolinite, were extracted and treated to become Na, K, Ca and Mg homoionic. The pH of homoionic clays was then adjusted accordingly. The effect of Mg on clay dispersion is compared to that of Ca. Similarly, the effect of K on soil clay dispersion is compared to monovalent Na, under similar pH conditions. A predictive model for dispersion is developed, and its applicability and limitations are discussed.

Chapter 5 investigates and discusses the specificity of Mg effect on the K_{sat} of three contrasting soils. The results are compared with Ca treatment at equivalent conditions. In addition, this chapter explores the interaction between Mg and soil organic matter by measuring the dissolved organic carbon from the collected leachate. Changes in K_{sat} were measured when the electrolyte concentration and composition of leaching solutions changed. Soil aggregate stability of water-leached samples were measured in order to assess the dispersibility of Mg soils. Mechanical tests on Mg and Ca soils were analysed together with the turbidity and zeta potential values. The specific effect of Mg as compared to Ca and the affecting factors are discussed.

Chapter 6 further validates the flocculating power of Mg as compared to Ca on seventeen soils. Soil clays were separated and prepared to be Na, K, Mg and Ca homoionic soil-clays. The excess electrolytes were removed using a dialysis method. The critical flocculated concentrations of homoionic soil clays were determined. The flocculation powers (mean, min, max and standard deviation) were calculated, and the sensitivity to these of CROSS and EDP were presented. The experimental results were compared to the flocculation power from Rengasamy and Sumner (1998), and the practical implications of the results presented.

Chapter 7 presents a general discussion of the previous chapters. The effect of Mg on soil clay dispersion and K_{sat} is discussed together with other influencing factors including clay mineralogy, pH, texture and organic matter. The effect of Mg on soil structural stability as compared to Ca is discussed specifically. The importance of the combined results, within the context of practical industry application and guideline development, are also presented. This chapter finalises by using the findings of this thesis and the key conclusions of this study to provide recommendations for future work.

The flow chart in Fig. 1–1 provides an overall schematic of the research. There is no doubt that the knowledge obtained in this thesis will form an important contribution to understanding the effect of Mg in soil structural stability. This knowledge will further facilitate the precise management strategies for increased productivity in magnesic soils.

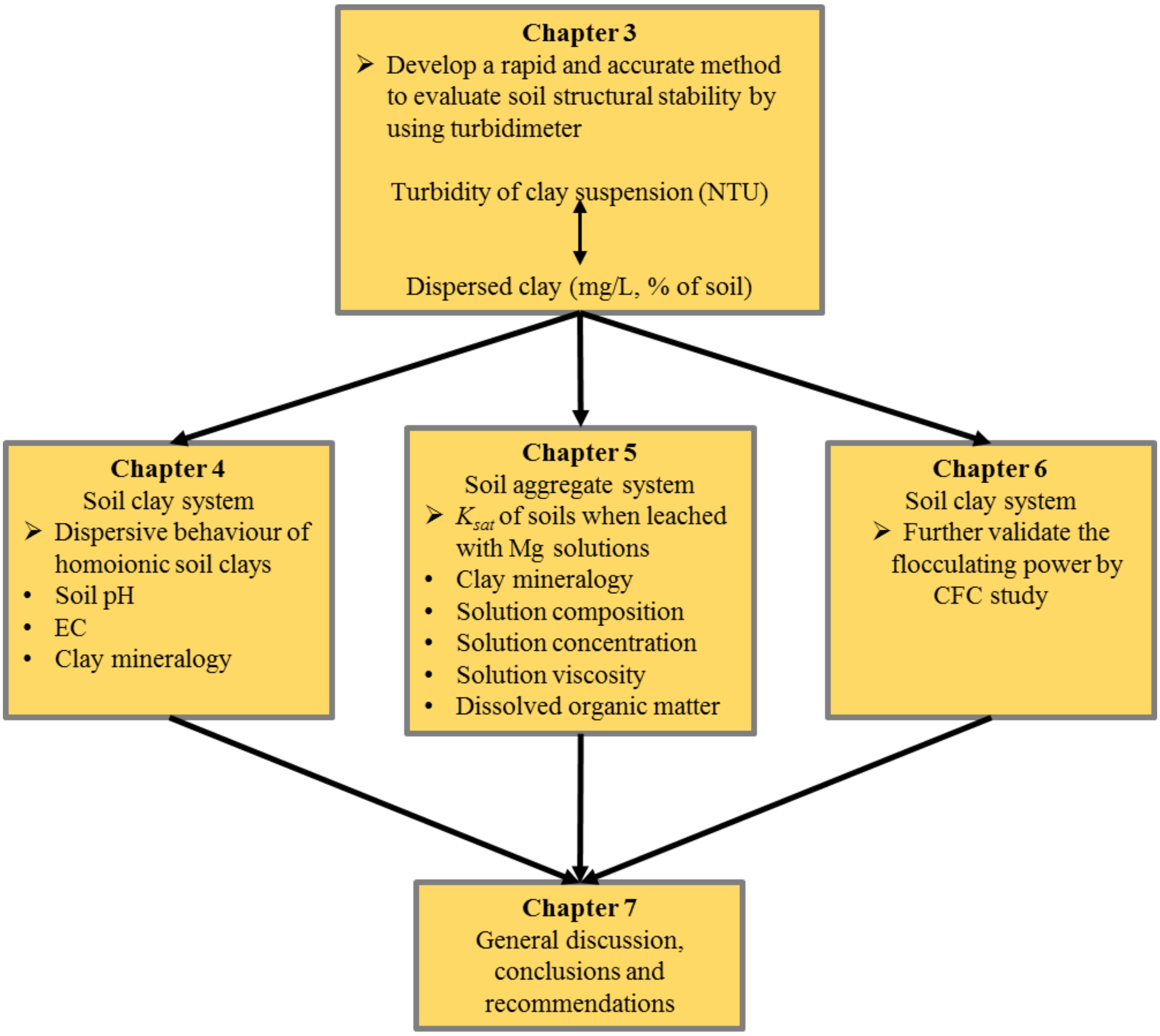

Fig. 1–1 Research flow chart of this thesis

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2. Literature review

2.1. Introduction

This chapter reviews the definition, distribution and formation of magnesic soils. Special attention is paid to the effect of Mg on soil structural stability and plant growth. In addition, this chapter discusses other soil physical and chemical properties which could affect soil structural stability, such as clay mineralogy, particle size, clay content, the nature of exchangeable cations, pH, electrolyte concentration in the soil solution, organic matter and mechanical stresses. These factors and their interactions determine soil structural stability and clay dispersive behaviour in magnesic soils. Furthermore, a number of theories are reviewed to understand clay dispersive behaviour, including the DLVO (Derjaguin, Landau, Verwey and Overbeek) theory, specific ion effect and ionicity concept. In the end, the soil structural dynamics, as affected by the processes of wetting a dry soil aggregate, are discussed.

2.2. Definition, distribution and formation of magnesic soil

2.2.1. Current definitions of magnesic soil

The definition and diagnostics of magnesic soils are not sufficiently elaborated and have been given less attention than other salt-affected soils (Szabolcs, 1989). In general, magnesic soils are known to be under the strong influence of magnesium compound, which contain increased amounts of mobile magnesium in soil solution and/or on the exchange sites (Szabolcs, 1989).

The variety of definitions of magnesic soil are summarized in Table 2–1. It is noted that there is no single agreed upon definition of magnesic soil, although several indices/parameters have been used to define magnesic soil; these include: exchangeable Ca/Mg ratio (or exchangeable Mg/Ca ratio) (Isbell, 1997; 2016; Podwojewski, 1995; Podwojewski and Beaudou, 1991); exchangeable magnesium percentage (EMP, the amount of exchangeable Mg as a proportion of the sum of exchangeable sodium (Na), potassium (K), calcium (Ca) and magnesium) (Garcia-Ocampo, 2003; Wang et al., 1993); and soluble Ca/Mg ratio (Rengasamy et al., 1986; Rengasamy et al., 1984; Yuan et al., 2007).

Table 2–1 Summary of definitions of magnesic soil

Terminology	**Index**	**Ca/Mg ratio Limits**	**Reference**
Calcimagnesic soil	Exchangeable Ca/Mg ratio	0.33–0.5*	Podwojewski (1995)
Magnesic soil	Exchangeable Ca/Mg ratio	0.1–0.33*	Podwojewski (1995)
Hypermagnesic soil	Exchangeable Ca/Mg ratio	<0.1*	Podwojewski (1995)
Magnesic/ Magnesic-Natric	Exchangeable Ca/Mg ratio	<0.1	Isbell (1997; 2016)
Alkalized magnesic soil	Soluble Ca/Mg ratio	<0.33	Yuan et al. (2007)
Soil degradation-magnesic soil	Soluble Ca/Mg ratio	<1.0	Rengasamy et al. (1986)
Alkalized magnesic soil	Exchangeable Mg percentage	>80%**	Wang et al. (1993)
Soil degradation-magnesic soil	Exchangeable Mg percentage	>40%**	Garcia-Ocampo (2003)
Soil degradation-magnesic soil	Exchangeable Mg percentage	>25%	Karajeh et al. (2004)
Magnesium soil	Soils develop under the strong influence of magnesium salts	–	Szabolcs (1989)

*Mg/Ca ratios have been converted to Ca/Mg ratios for ease of comparison.
**Expressed as percentage of the cation exchange capacity, rather than Ca/Mg ratio.

These different parameters have been used to define magnesic soils within specific contexts, although the applicability of the limits is likely to change with direct regard to soil structural stability. Rengasamy et al. (1986) suggested that as the ratio of soluble Ca/Mg reduces below 1.0 dispersion can be induced in a range of red-brown earth soils, while the Australian Soil Classification (Isbell 2002) indicates a soil as magnesic where the exchangeable Ca/Mg ratio is less than 0.1. Several authors have used EMP to describe magnesic soil, due to the fact that Mg saturation in the exchange complex can largely determine soil chemical and physical properties (Garcia-Ocampo, 2003; Li et al., 2012; Wang et al., 1993). Alkalized magnesic saline soils are characterized by high Mg and alkalinity (EMP >80% and pH >9.0) and high total salinity (Wang et al., 1993), while soils with an EMP >40% are referred as magnesic soils in Colombia (Garcia-Ocampo, 2003). The presence of high total salinity would likely change the structural behaviour under the definition proposed by Wang et al. (1993), and it might be considered that, if the salinity was lowered, the EMP threshold demonstrated by Garcia-Ocampo (2004) could hold. In addition, studies undertaken in the Amu-Darya and Syr-Darya River Basins in Uzbekistan and Kazakhstan reported that soil structure degradation was found in most soils with EMP >25% by restricted infiltration rates and low hydraulic conductivities. These soils also form massive clods when they dry in the post-irrigation phase (Karajeh et al., 2004; Qadir et al., 2018). However, Bennett et al. (2016) mathematically derived an effectiveness term for Mg and its contribution to soil instability, suggesting that the percentage of the cation exchange complex occupied by Mg, and the Ca/Mg ratio needed to be considered together. They concluded that the use of the Ca/Mg ratio alone was insufficient as an adverse Ca/Mg ratio (adverse by standard of any definition in Table 2–1) could exist with very low

EMP, meaning the ratio might be adverse but have no practical effect on soil structure. Therefore, it is apparent that a better definition of Mg’s effect on soil structure is required.

The diversity of definitions among different regions is likely due to the contextual reasoning of the limits and the fact that magnesic soils with different properties are included in a single group, regardless of the soil forming processes, the sources and manner of Mg enrichment, and the type and mobility of Mg compounds accumulated. Therefore, when discussing the influence of Mg on soil properties, the types and sources of Mg compounds must be clarified, as well as the intended context of the constraints. In this thesis, soils with high concentrations of Mg either in the soil solution or the exchange complex are considered magnesium affected. The inclusion of a numeric threshold has been resisted, as it is the purpose of this thesis to investigate the effects of Mg on soil dispersion and disaggregation.

2.2.2. Distribution of magnesic soil

As noted, the diagnostics of magnesic soils are not sufficiently discussed. To the author’s best knowledge, there is no detailed mapping on the distribution of magnesic soils. Part of the reason is because some researchers have studied the magnesic soils in combination with sodic, alkali and/or saline soils. In recent years, magnesic soil have been reported in many countries where formerly they were unknown/ignored, and it is likely that more information of the discovery of Mg affected soils will be available in different areas in the future (Qadir et al., 2018). The recognition of significance and importance of magnesic soil is growing continuously, which can be explained primarily by their distribution on all continents, albeit without detailed mapping having occurred.

South America

In Colombia, a large area of soils with high amount of Mg in soil solution and exchange complex has been found, located mainly in the major river valleys and in the Caribbean Region. There are about 117,000 ha affected by the accumulation of Mg on the exchange complex in the Cauca River Valley (Garcia-Ocampo, 2003). In Argentina, magnesic soils are found in several cases in association with alkali soils (Szabolcs, 1989).

North America

Magnesic soils are found in some regions within Canada. In the Sumas region in the Lower Fraser Valley, the soils have been affected by serpentinic sediments and have higher values of exchangeable Mg in comparison to Ca, notably in the lower solum (Baugé et al., 2013; Luttmerding, 1981). The magnesium affected soils in the United States are extensive, partly as the result of a high magnesium content in groundwater (Szabolcs, 1989). In the U.S.A., magnesic soils derived from serpentine materials occur in at least three orders, five suborders, and six great groups (Bockheim, 2005).

Europe

The extent of magnesic soils in Europe is limited (Szabolcs, 1989). Nevertheless, magnesium affected soil can be found in the mountainous parts of Romania (Szabolcs, 1989). These soils contain mainly magnesium sulfate, either present in small depressions or on the site of geological salt accumulation.

Africa

Magnesic soils are found in many places in Africa, which is related to the lithology and mineralogy of these areas. It is noted that magnesic soils are frequently associated with the occurrence of alkali soils, such as in Sudan (Szabolcs, 1989). Magnesium affected soils are also reported in Egypt (Moslehuddin and Egashira, 1997; Rabie and El-Araby, 1979) and Tanzania (Bennett et al., 2016a).

Asia

The soils from alluvial fans and basins in arid regions of north-western China (Gansu-Xingjiang) are characterized by a significant accumulation of magnesium carbonate with wide distribution of sodic soils (Wang et al., 1993). In the coastal areas of India, saline soils have chlorides and sulphates as dominant anions and Na as the dominant cation, though appreciable amounts of Mg can be present in some cases. In the Kazakhstan part of the Aral Sea Basin, Western Asia, more than 140,000 ha had irrigation water containing higher concentrations of Mg than Ca. Consequently, more than 30% of the irrigated area in southern Kazakhstan is dominated by soils that have an EMP in the range of 25–45%, and in some cases as high as 60% (Vyshpolsky et al., 2010). Magnesic soil are also reported in Iraq, Iran, Afghanistan, etc (Buringh, 1960; Ghasemi et al., 2015; Szabolcs, 1989).

Oceania

Magnesium rich soils cover large areas in New Caledonia, especially on the western dry coast (Podwojewski, 1995). In Australia, magnesium ions may accumulate in the soils in river valleys, lowland terraces, and other places where the ground water is linked with the soil profile due to hydromorphic processes (Szabolcs, 1989). A comparison of exchangeable cation data from a Mg-containing sodic soil at Condobolin, New South Wales, Australia, reveals ratios between exchangeable Ca and Mg around 1 and an EMP around 40 % (McKenzie et al., 1993). By reviewing the status of exchangeable cations in Australian soils, a large proportion of soils have a comparatively high exchangeable Mg content as compared to the United States (Tucker, 1983). Similar reported results indicate that many Australian soils contain high proportions of Mg in the exchangeable cations, especially in the subsoil (Qadir and Schubert, 2002). In a study of 91 acidic Queensland soils, 1% of surface soils and 10% of subsoils had exchangeable Mg >6 cmol_c/kg, which is considered fairly high (Bruce et al., 1989). Furthermore, 7% of Sodosol soils had Ca/Mg ratios less than 0.1 in the major part of the B2 horizon (Isbell, 1997; 2016), and Sodosols account for 13.0% of Australian soils. Magnesic soils are found in Kurosols (40%), Hydrosols, Vertosols, Chromosols (3%), Dermosols (6%), Ferrosols (3%) and Kandosols (5%) within Australia (Isbell, 1997; 2016); the percentage in the brackets being the frequency of magnesic soil to that soil order. Magnesic soils are found in Australia partly associated with saline soils in dry areas, where magnesium sulphate and, to some extent, magnesium chloride are found in the upper soil layers, and are likely to be associated with soils formed on marine sediments (Van Voast, 2003). Moreover, magnesic soils are partly associated with alkali soils and sodic soils (Szabolcs, 1989).

2.2.3. The sources and formation of magnesic soil

The magnesium in soils presents in different forms, and the concentration of Mg amongst the various forms varies widely. In general, the majority of Mg (about 71%) is in the mineral pool, a smaller amount of Mg is in exchangeable and soluble forms, and a trace amount is associated with organic matter (Fageria, 2008; Hailes et al., 1997; Mokwunye and Melsted, 1972; Salmon, 1963). This thesis is concerned with Mg in exchangeable and soluble forms, as Mg present in these two forms is easily accessible as nutrition for plants. In addition, if Mg in these two forms is present in appreciable amounts and/or in combination with monovalent cations such as Na and K, it may directly affect soil structural stability. The sources of elevated concentration of Mg in soil solutions and on the exchange complex are:

1. *Pedogenic processes:* Weathering of parent minerals contributes to the formation of magnesic soil (Burt et al., 2001). Table 2–2 presents principal magnesium–containing soil minerals, their composition and considerable variations in Mg content between different minerals. The highest Mg content is derived from serpentine material with up to 490 g/kg. The magnesic Vertosols, found in central Queensland were originally derived from serpentine material (Foster and Baker 1996). In the U.S.A., magnesic soils derived from serpentine materials occur in at least three orders (Alfisols, Mollisols,

Inceptisols), five suborders, and six great groups (Bockheim, 2005). In addition, substantial sources of Mg can be brucite ($Mg(OH)_2$), carbonates (*e.g.* magnesite ($MgCO_3$) and dolomite ($MgCO_3 \cdot CaCO_3$)) and magnesium sulphate ($MgSO_4$); even naturally formed calcite ($CaCO_3$) is known to contain 1–3% Mg (Gransee and Führs, 2013). Furthermore, variation in Mg content can be found in minerals. The reason is that within the silicates the Al^{3+} is substituted by Mg^{2+}. This well described phenomenon (isomorphic substitution) causes surface permanent charge, which is also critical for the physical and chemical properties of soils (Grim, 1939; Nadeau, 1985; Sposito, 2008).

The nature of clays and the solubility of predominant minerals play important roles in Mg enrichment of the soils (Garcia-Ocampo, 2003). With increasing soil maturity there is a tendency towards increasing EMP compared with calcium (Higashi, 1961; Metson, 1974). This is because magnesium is a lattice constituent of the 2:1 clay (detailed in Section 2.4.1), substituting for aluminium in octahedral layers, whereas calcium is not a lattice constituent. Hence, once the calcium-bearing primary minerals are decomposed, almost all the calcium cations present are in an exchangeable form (Higashi, 1961). Thus, the exchangeable Ca/Mg ratio tends to decrease in strongly leached, strongly weathered soils due to a greater presence of Mg (Metson, 1974).

Table 2–2 Principal magnesium-containing soil minerals and their composition (Fageria, 2008)

Soil Mineral	**Formula**	**Mg Content ($g \cdot kg^{-1}$)**
Magnesium sulphate	$MgSO_4$	200
Magnesium carbonate	$MgCO_3$	290
Serpentine	$H_4Mg_3Si_2O_9$	490
Dolomitic lime	$CaCO_3 \cdot MgCO_3$	130
Montmorillonite	$Al_5MgSi_{12}O_{30}(OH)_6$	Up to 60
Illite	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	20
Vermiculite	$Mg_3Si_4O_{10}(OH)_{2.2}H_2O$	120–170
Chlorite	$Al_2Mg_5Si_3O_{10}(OH)_8$	Up to 230
Brucite	$Mg(OH)_2$	410

2. *Irrigation:* Irrigation waters with high concentrations of Mg can accumulate magnesium in soil systems. Such systems take the groundwater ions, leached through thousands of years in to aquifers, and reapply these at the surface, resulting in concentration near the surface. Overland flow can subsequently move Mg into freshwater reserves, augmented by the release of industry waste-waters and the dissolution of soil additives containing Mg. There are emerging data from irrigation schemes worldwide showing high levels of Mg in irrigation waters resulting in its accumulation in soils. For

example, in Israel, the irrigation waters from the National Water Carrier with Ca/Mg ratio of 1:1 and from some saline waters of the western Negev with Ca/Mg ratio of 1:3, result in large increase in exchangeable Mg in the soil (Alperovitch et al., 1981). In Queensland coastal areas, magnesic-sodic groundwater has been used for irrigation in sugarcane growing areas for decades, with one example demonstrating that ground water irrigation has resulted in 68% exchangeable Mg in the top 0–25 cm layer of a Vertosol (Skilton et al., 2000). In Southern Kazakhstan, such as Arys Turkestan Canal command zone, some irrigation water (canal water) contains high levels of magnesium with the Ca/Mg ratio <1.0. After 30 years of intensive irrigation and excessive leaching, more than 30% of the irrigated lands in Southern Kazakhstan have EMP values in a range of 25–45%, and in some cases as high as 60% (Karimov et al., 2009; Vyshpolsky et al., 2010; Vyshpolsky et al., 2008). In India, a sizeable number of waters contained Ca/Mg ratio as low as 0.1 in Uttar Pradesh, and the Mg concentration on the exchange complex increased substantially through irrigation (Vishnoi, 1985).

3. *Soil additives:* Some amendments, such as dolomite ($CaMg(CO_3)_2$), can increase magnesium concentration in soils. In the main corn and soybean producing regions in the Midwest U.S.A., farmers often prefer to apply dolomite as a liming material on acidic soils rather than using calcitic limestones, because of the widespread, less expensive and acid neutralization capacity of the former (Dontsova and Norton, 1999). Hence, the application of dolomite introduces Mg into soil solution and exchange sites. In Australia, dolomites have been recommended to increase pH of acidic soils as well (Queensland Government, 2009). This is likely to increase magnesium levels in soil solution and on exchange sites.

Whilst these three factors contribute to the formation of magnesic soils, the consequence for soil condition is less well understood. For example, the use of dolomite on soils was initially considered directly equivalent to the use of calcite in terms of its effect on soil structure. This was due to an assumption that Mg and Ca, as divalent ions, had equivalent effect in flocculating soils. However, the body of work surrounding the Mg effect on soil since the 1980s suggests this requires further investigation, and that soil-specific effects related to Mg concentration are likely (Bennett et al., 2016a).

2.2.4. The concentration of Mg in soil is dynamic

The concentration of Mg in a soil system is dynamic. Accumulation/replenishment of Mg happens via pedogenic processes, irrigation and application of soil additives, while Mg losses occur due to water leaching, plant uptake or even Mg fixation (Bolton, 1973; Metson, 1974; Schroeder et al., 1963; Ståhlberg, 1960). For arable crops the average uptake of Mg is approximately 10–25 kg·ha^{-1}yr^{-1} and, generally, the uptake by root crops is about double that of arable crops (Mengel et al., 2001). The leaching rates of Mg are extremely variable, ranging from 2–100 kg·ha^{-1}yr^{-1} for non-fertilised plots, and from 34–104 kg·ha^{-1}yr^{-1} for fertilised plots (Bolton et al., 1970). Sumner et al. (1978) and Grove et al. (1981) reported Mg fixation in Oxisols and Ultisols when limed to pH above 7.0. A small amount of replenishment of Mg can also occur through crop residues, farmyard or green manures, rainfall, etc., though it is unlikely to result in the formation of a magnesic soil. For example, assuming the crop yield is 10,000 kg/ha of dry matter, with a magnesium concentration of 0.3%, the total magnesium uptake would be 30 kg. If 20% (or 40%) of this returned to the soil, this would include 6 kg (or 12 kg) of Mg (Metson, 1974). It is clear that the Mg concentration in the soil has a dynamic that is associated mostly with management practices, specific soil types, and chemical reactions, with management practices considered to result in the most rapid dynamic change. Furthermore, this highlights that the concentration of Mg is quantifiable and manageable in the majority of situations.

2.3. The effect of Mg on soil structural stability and plant growth

The accumulation of Mg in the soil solution and exchange complex is expected to affect soil physical, chemical and biological properties. The optimum level is highly debated, with authors producing numerous conflicting reports (Alperovitch et al., 1981; Bennett et al., 2016a; Keren, 1991; Rahman and Rowell, 1979; Rengasamy et al., 1986), leading to the assertion that Mg has a specific effect. In magnesic soils, for which there is only limited information, the combination of toxic effect, calcium deficiency, and poor soil physical properties can be considered stress factors. This thesis is specifically focused on the structural stability of magnesic soils, as this is one of prerequisites for maintained and/or increased productivity. In this section, the significance of soil structural stability, and the effect of Mg on soil structural stability and plant growth are discussed.

2.3.1. The significance of soil structural stability

Soil structural stability describes the ability of the soil aggregates and their arrangement, to retain, or resist change in pore geometry when exposed to an external force (Amezketa, 1999; Bronick and Lal, 2005; Lal, 1991; Oades, 1984). One of the typical indicators of structural stability is aggregate stability (Amezketa, 1999; Six et al., 2000a). By observing the interaction between aggregates with water, *i.e.* slaking, swelling, disaggregation and clay dispersion, soil aggregates have been divided into different stability classes and stages (Emerson, 1967; Loveday and Pyle, 1973; Rengasamy and Olsson, 1991). Slaking can occur in a wide range of soils where the aggregates, on contact with water, are not strong enough to withstand the hydrostatic and pneumatic pressures of entrapped air in capillaries or the pressures due to intra-crystalline swelling, *i.e.* aggregates break into smaller aggregates (>2 μm) (Rengasamy and Olsson, 1991; Tisdall and Oades, 1982). Dispersion occurs when these small aggregates produced by slaking are unstable due to repulsive forces in the clay domain, causing individual clay particles to dislocate from the clay domain under Brownian motion (Quirk, 2001). Separation of individual particles (clay particles <2 μm) has traditionally been documented as occurring in sodic soil, which have high exchangeable Na content (Rengasamy and Olsson, 1991; Tisdall and Oades, 1982). Between the states of absolute stability and dispersion the soil aggregate is in a state of disaggregation, but does not spontaneously disperse. This was initially referred to as inter-crystalline swelling by Quirk and Schofield (1955) and is explained by the development of diffuse double layer (DDL) expanding the clay domain as the attractive forces are overcome by increasing repulsive force.

Slaking, swelling, disaggregation, dispersion and their combination degrade soil structure. Soil structural stability as affected by sodicity is illustrated in Fig. 2–1. In the field, slaking of aggregates occurs mainly in surface layers, which may limit infiltration of water and emergence of seedlings (Tisdall and Oades, 1982). In some circumstances, slaking is considered to be the major cause of reductions in hydraulic conductivity (Abu-Sharar et al., 1987). Soil swelling reduces pore sizes (Frenkel et al., 1978; Zhang and Norton, 2002). Clay dispersion followed by migration of clay particles and plugging of water-conducting pores is regarded as one of the major processes causing structural problems in irrigated soils (Curtin et al., 1994a). In most cases, structural instability leads to undesirable soil properties such as poor drainage, surface crusting, hard setting and poor workability, which eventually reduce crop yield (So and Aylmore, 1993).

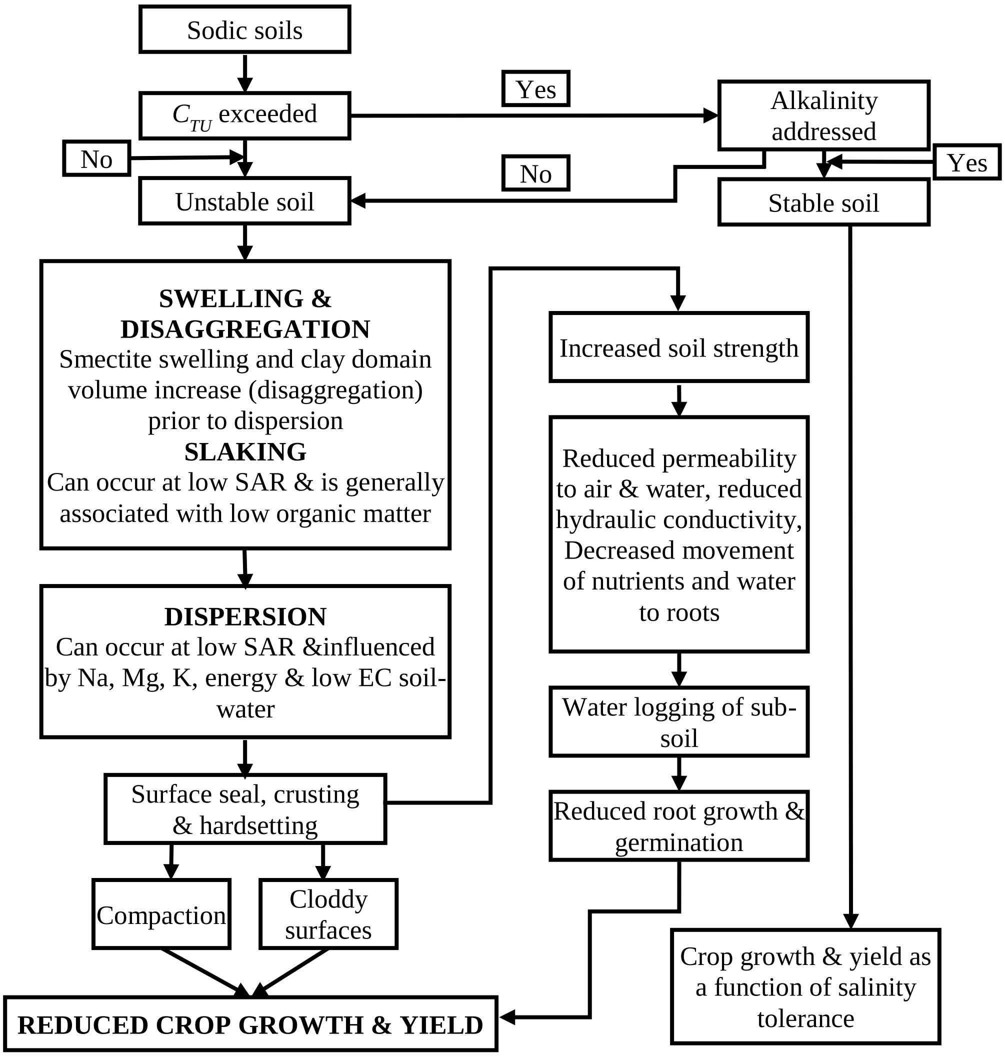

Fig. 2–1 Soil stability as affected by sodic soils and the effects on productivity as governed by changes in soil structure (Modified from So and Aylmore (1993)). SAR, sodium absorption ratio; C_{TU}, threshold electrolyte concentration.

2.3.2. The effect of Mg on soil structural stability

With respect to the effect of Mg on soil structural stability, different perspectives have been reported. US Salinity Laboratory Staff (1954) grouped Mg and Ca together as having similar beneficial effects on soil structure. However, it is known that an increase in the concentration of Mg in soils or irrigation waters can increase dispersion, reduce hydraulic conductivity of soil and cause structural deterioration (Bakker and Emerson, 1973; Curtin et al., 1994b; Dontsova and Norton, 1999; Emerson and Chi, 1977; Keren, 1991; Rengasamy et al., 1986). The direct effect of Mg in decreasing structural stability is termed the ‘specific effect of Mg’ (Curtin et al., 1994b).

Bohn et al. (2002) reported that high exchangeable Mg is sometimes associated with low water permeability, soil crusting and high pH, and is similar to the characteristic conditions of sodic soils. Rahman and Rowell (1979) found that Na-Mg montmorillonite pure clay and Na-Mg montmorillonite soil behaved similarly to their Na-Ca counterparts at the same exchangeable sodium percentage (ESP) and electrolyte concentration in terms of clay swelling, clay dispersion and hydraulic conductivity (K). However, Rahman and Rowell (1979) reported in the same paper that Na-Mg illitic soil and mixed illite-montmorillonitic soil had greater reduction in K than in Na-Ca systems, suggesting that Mg has a specific effect on illitic, but not montmorillonitic soil. In contrast, Keren (1991) found the adsorbed Mg ions to have a specific effect on soil erosion and infiltration rates for montmorillonitic soils. Dontsova and Norton (1999) studied the influence of modified Ca/Mg ratios on surface sealing of four soils from Midwestern U.S.A., which are non-sodic soils, and their results showed that Mg had a specific effect on soil clay flocculation and surface sealing. Zhang and Norton (2002) studied two humid region soils containing smectite, kaolinite, vermiculite and illite, and confirmed that Mg had a specific effect compared with Ca on aggregate stability, clay dispersion and saturated hydraulic conductivity (K_{sat}). These results demonstrated the effect of Mg on structure is specific in terms of clay mineralogy, and the degree to which it decreases structural stability needs further investigation.

There is no general consensus in quantifying the effect of Mg on soil structural stability. Curtin et al. (1994b) reported that the exchangeable Mg had a specific effect on clay dispersion, and suggested that exchangeable Mg is about 4 to 5 % as effective as exchangeable Na in terms of dispersibility. Emerson and Chi (1977) suggested that Mg enhanced the dispersion of illite as compared to Ca, and deduced that Mg was about one-tenth as effective as an equivalent amount of exchangeable Na in causing dispersion. It is often observed that the presence of Na in soil systems obscures the Mg effect. Consequently, different observations regarding the existence of a specific Mg effect are partially due to the difficulties of excluding the specific effect of Na. Thus, it would be prudent to investigate the specific effect of Mg in homoionic soil clay systems, rather than mixed cation systems.

A number of investigations have attempted to explain the deleterious effect of Mg on soil aggregate stability and hydraulic conductivity as shown in Table 2–3. As compared to Ca, Mg has greater hydration radius and energy, which causes a larger separation distance between clay layers and less attraction between them to cause flocculation (Bakker et al., 1973; Dontsova and Norton, 1999; Zhang and Norton, 2002). Keren (1991) attributed the lower energy required to break down Mg soil aggregates compared to Ca aggregates to the wider hydration shell of the Mg ions. Curtin et al. (1994b) and Emerson and Chi (1977) reported that the electrostatic force by which the Mg ion is held to the soil surface is less than that of Ca, so that a greater proportion of ions can dissociate from the exchange sites in the Mg system. Therefore, the repulsive forces, which are responsible for the dispersion, are somewhat greater in the Mg system (Curtin et al., 1994b; Emerson and Chi, 1977). Astaraei and Chauhan (1992) observed Na on the exchange complex to increase with decreasing Ca/Mg ratio of water (clay fraction was dominated by illite). The ESP, Na/(Ca+Mg) ratio and degree of dispersed clay in soil were all found to increase with increasing concentrations of Mg at certain levels of electrical conductivity and SAR. The authors attributed this to the greater affinity of Ca to soil when compared with Mg, and hence easier replacement of Mg by Na. Furthermore, some authors attributed the different effects of Mg on soil dispersion behaviour to the existence of carbonate in soil. Alperovitch et al. (1981) reported that exchangeable Mg had a specific effect on the hydraulic conductivity and clay dispersion in noncalcareous soils but no specific effect in calcareous soils. The authors suggested that in non-calcareous soils, exchangeable Mg can stabilize the structure and prevent the mineral dissolution of the soil clays. In consequence, the electrolyte concentration of the soil solution with Mg-soil is low and hydraulic conductivity drops. Conversely, clay dispersion and reduction in hydraulic conductivity of soil is prevented in calcareous soils where exchangeable Mg enhances the dissolution of the carbonates and increases electrolyte concentration. However, the effect of Mg concentration on the precipitation or dissolution of carbonate is a complex function (Hassett and Jurinak, 1971). It depends not only on the surface area of calcite, but also depends on the amount of Mg in the carbonate mineral. Later, Shainberg et al. (1988) suggest the lower electrical conductivity of Na-Mg systems relative to Na-Ca systems are related to the effect of Mg on the hydrolysis of these clays. The presence of a high concentration of Mg at the clay surface slowed down the release of octahedral Mg from the hectorite (smectite) lattice and lowered the electrical conductivity of the Na-Mg clay. Exchangeable Mg did not inhibit hydrolysis in the soils containing kaolinite because of the limited isomorphic substitutions in kaolinite where very small amounts of octahedral Mg is in the crystal (Levy et al., 1989).

Table 2–3 The summarized mechanism of Mg instability and the extent of its effect

Mechanism of instability	Extent of effect	Reference
Mg has greater hydration radius and hydration energy than Ca.	Lower infiltration rates in Mg soils than Ca soils. In the presence of Na, Ca aggregates were more stable than Mg aggregates.	Keren (1991)
	Mg had a specific effect on soil clay flocculation and surface sealing. The erosion rate of the soils was higher for the Mg soils than for the Ca soils.	Dontsova and Norton (1999)
The electrostatic force with which Mg ions are held at the clay surface is less than that of Ca, thus the repulsive forces are greater in the Mg system.	Mg was about 3% as effective as exchangeable Na in causing dispersion on an illitic red-brown Earth soil.	Emerson and Bakker (1973)
	Mg illites showed higher dispersion than Ca ones. Mg was about 10% as effective as Na in causing dispersion.	Emerson and Chi (1977)
	Na-Mg soil systems had lower K than the corresponding Na-Ca system. Mg produced about 4% to 5% of the dispersive effectiveness of Na.	Curtin et al. (1994b)
Ca has greater affinity to soil, as compared with Mg, and hence facilitate easier replacement of Mg by Na.	Increase in Na on the exchange complex with decreasing Ca: Mg ratio solution.	Astaraei and Chauhan (1992)
Exchangeable Mg enhances the dissolution of the carbonates and increase in electrolyte concentration, thus clay dispersion and reduction in hydraulic conductivity of soil is prevented in calcareous soils.	Exchangeable Mg had a specific effect on the hydraulic conductivity and clay dispersion in non-calcareous soils but no specific effect in calcareous soils.	Alperovitch et al. (1981)
Exchangeable Mg slowed down the release of octahedral Mg from the smectite lattice and lowered the EC. This mechanism became dominant when the electrolytes in the solution were mainly derived from the hydrolysis of the clay minerals.	Compared with Ca counterparts, Mg showed direct effect on the hydraulic conductivity of smectite-sand mixtures that were equilibrated with certain SAR values and leached with distilled water.	Shainberg et al. (1988)
Mg had lower flocculation power than Ca by considering the combination effect of Misono factor, ionic potential and valence.	Mg clays had lower critical flocculation concentrations than Ca clays. Mg was considered to be 3.7% as effective as Na in causing dispersion, and 60% as flocculating effective as Ca.	Rengasamy and Sumner (1998)

Rengasamy and Sumner (1998) theoretically derived the flocculating power (Eq. 2.1) of the major cations (*i.e.* Ca, Mg, Na, K) by combining the Misono softness parameter and the ionic valence factor. They calculated that if the flocculating power of Na=1, the flocculating power of the other cations would be K=1.8, Mg=27, and Ca=45, which were further verified experimentally by using clays extracted from four different soils from Australia, S. Africa, Nigeria and Georgia, USA.

$$Flocculating\ power = 100\left(\frac{I_Z}{I_{Z+1}}\right)^2 Z^3 \qquad \text{(Eq. 2.1)}$$

In equation 2.1: Z is the valence of the cation, the ionisation potential of which is I_Z, and I_{Z+1} is the ionisation potential when the valence of the cation changes to $Z+1$.

Flocculating power gives the reverse of dispersive effects. Based on this concept, Rengasamy and Marchuk (2011) proposed the cation ratio of structural stability (CROSS, Eq. 2.2) as an index which would be analogous to SAR, but incorporated the differential effects of Na and K in dispersing soils, and the differential effects of Ca and Mg in flocculating soil clays.

$$CROSS = \frac{[Na^+] + 0.56[K^+]}{\sqrt{0.5([Ca^{2+}] + 0.6[Mg^{2+}])}} \qquad \text{(Eq. 2.2)}$$

In equation 2.2, the concentrations of these ions are expressed in mmol of charge per litre.

Smith et al. (2015) verified the coefficients based on clay dispersibility which improved the correlation between CROSS and threshold electrolyte concentration (C_{TU}) for a Sodosol soil. The authors also postulated a more general definition of CROSS which produced a better correlation with C_{TU} for the Sodosol soil through optimization of the two coefficients using irrigation water composition data. Based on their findings, the deleterious effect of K is about one-third of that of Na and the concentration of Mg needs to be about 13 times larger than Ca to have the same beneficial effect. On this basis, the coefficients for K and Mg may need to be adjusted for different soils due to different clay mineralogy and other factors (Smith et al., 2015).

Currently, Australian soils are considered non-sodic or non-dispersive when the soil ESP is <6. However, some studies have demonstrated that K ions on the exchange complex of soil can also assist clay dispersion, even when the exchangeable Na levels are minimal. Marchuk (2014), using 17 soils from 17 locations around Australia, demonstrated that those soils were dispersive with an ESP less than 5. The relationships between ESP and turbidity were poor (R^2=0.23) indicating limitations of using the ESP for identifying potentially dispersive soils when K is present on the soil exchange sites. The authors suggested to take into account the effects of K on clay dispersion by proposing exchangeable cation ratio (ECR, Eq. 2.3) as an alternative to ESP.

$$ECR = \frac{[Na^+] + 0.56[K^+]}{[Na^+] + [K^+] + [Mg^{2+}] + [Ca^{2+}]} \times 100 \qquad \text{(Eq. 2.3)}$$

However, ECR does not account for the dispersive effects of exchangeable Mg cations. Bennett et al. (2016a) using two data sets of soils where K and Mg dominated the Cation exchange capacity (CEC), demonstrated Mg is less effective than Ca as a clay flocculant, but contributed little to dispersion. CEC is the measure of the total capacity of a soil to hold exchangeable cations, usually as a sum of exchange Na, K, Mg and Ca. Based on the flocculating power of cations, Bennett et al. (2016a) calculated the dispersive equivalent of Mg to Na, on this basis that the exchangeable dispersive percentage (EDP, Eq. 2.4) was derived and proposed to replace ESP and ECR (Bennett et al., 2016a).

$$EDP = \frac{[Na^{+}] + 0.556[K^{+}] + 0.037[Mg^{2+}]}{[Na^{+}] + [K^{+}] + [Mg^{2+}] + [Ca^{2+}]} \times 100 \qquad \text{(Eq. 2.4)}$$

In Equation 2.4, the concentrations of these ions are expressed in $\mathrm{cmol_c kg^{-1}}$.

To date, there is a growing trend in using CROSS and EDP indices to evaluate soil structural stability (Emami et al., 2014; Laurenson et al., 2011; Mosley et al., 2017; Qadir et al., 2018; Smith et al., 2015). However, one must also note that the coefficients in CROSS and EDP indices were derived from flocculation powers, which were verified in a limited number of soil clay system. Therefore, before this relationship can be generally used, further validation is necessary.

2.3.3. The effect of Mg on plant growth

Magnesium is an essential macronutrient for plant growth and development as it plays the role of enzyme activator and is a constituent of chlorophyll (Fageria, 2008; Weil and Brady, 2016). It has been recognized that long-term unbalanced crop fertilization practices without consideration for Mg depletion of soils leads to Mg deficiency in plants, consequently decreasing plant productivity and quality (Gransee and Führs, 2013).

On the other hand, like other metals, Mg at high levels can affect the colonization and growth of plants and hence, plant productivity (Yang et al., 2014). Exchangeable Mg in soils formed on serpentine rock is typically 3 to 9 times more abundant than Ca, which can cause severe Ca deficiency and Mg toxicity, allowing few plant species to grow in this unique environment (Weil and Brady, 2016). Poor plant growth on alkalized magnesic saline soils has been observed often (Li et al., 2012; Liu, 1985; Yuan et al., 2007). High concentration of Mg reduces the initiation, density and length of root hairs in *Arabidopsis* (Niu et al., 2014a; Niu et al., 2014b). Yield depression of corn was reported when irrigated with low Ca/Mg ratio waters, as compared to the yield obtained with tap water, where the corn was grown in the greenhouse in a calcareous soil (Franklin et al., 1991). However, contrasting results have been reported. The Ca/Mg ratio has been observed unimportant for plant growth, as the yield was not well predicted by Ca/Mg ratios ranging from 1:4 to 32:1 (Fox and Piekielek, 1984; Liebhardt, 1981; Qadir et al., 2018). Indeed, in soils with high Mg content, low yield could result from a Ca deficiency rather than an "excess" of Mg (Kopittke and Menzies, 2007). In summary, either Mg toxicity due to high concentration or Ca deficiency can inhibit plant growth. This should be considered and clarified when assessing yields from magnesic soils.

2.4. Other factors affecting soil structural stability

In addition to the specific effect of Mg, there are other factors that can affect structural stability of magnesic soils. In general, the degree of soil dispersion is determined partly by composition of exchangeable cations in the soil (particularly Na fraction) and electrolyte concentration (Curtin et al., 1994a; Quirk and Schofield, 1955). More factors that affect soil dispersive behaviour include clay content and mineralogy (Frenkel et al., 1978), clay particle size (Sides and Barden, 1971), sesquioxides (Goldberg and Glaubig, 1987), soil pH and EC (Goldberg and Forster, 1990). The mechanical stress applied to soil also affects the dispersive behaviour (Curtin et al., 1994a). These factors and their effects on soil structural stability are reviewed and discussed in this section.

2.4.1. Clay mineralogy, particle size and content and their effects on soil structural stability

Soil consists of a range of sizes of mineral particles (sand, silt and clay) and organic matter. The finest fraction of mineral particles, clay (usually <2 µm), contributes the largest proportion of surface area of soil, supplies nearly all the charge and dominates the chemical composition and physical properties, *e.g.*, soil dispersibility (Churchman, 2006). The clay minerals in soils largely consist of aluminosilicates as well as a range of sesquioxides (Churchman et al., 1993). Kaolinite, illite and smectite (particularly montmorillonite) are the most common minerals presented in soils (Churchman et al., 1993; Norrish and Pickering, 1983). The surface area, cation exchange capacity, charge origin and density, morphology and size of clay minerals are critical in influencing their dispersive behaviour.

2.4.1.1. Clay mineral structure and origin of charges

The crystal structure of the aluminosilicate layers, in detail, consists of sheets of tetrahedral silica (T sheet) in combination with sheets of octahedral alumina or magnesia (O sheet), forming different layer ratios of 1:1 and 2:1 of T and O layers, respectively (Swartzen-Allen and Matijevic, 1974). A negative layer charge arises from isomorphic substitution whereby ions substitute for others of comparable size, irrespective of valence, during the formation of a mineral crystal without disrupting the growth of crystal structure (Singer and Munns, 2006). Although isomorphic substitution is the main source of the negative charge of clay particles, the absence of a constituent metal atom from the clay crystal structure, and the broken bonds at the edges of the particles also attribute to the negative charge (Bergaya et al., 2006b; Swartzen-Allen and Matijevic, 1974).

A 2:1 clay structure (TOT structure), such as montmorillonite and illite, consists of a sheet of octahedral alumina (or magnesia) between two sheets of tetrahedral silica. In montmorillonite (Fig. 2–2), substitution of trivalent cations (commonly Al^{3+} and Fe^{3+}) for Si^{4+} in tetrahedral sites results in negative charge. Furthermore, substitution of divalent cations for trivalent cations in the octahedral layer also results in negative charge on the layer. However, when the substitutions occur in the tetrahedral sites, the lattice charge deficiency has its origin ≈0.2 nm from the surfaces of the silicate layers, whereas substitutions in the octahedral sites originate ≈0.47 nm from the surfaces (Slade and Quirk, 1991). If the clay charge is generated in tetrahedral positions, the attractive electrostatic force between the interlayer cations and the surface will be greater than if the charge is generated in the more deeply buried octahedral positions (Slade et al., 1991). Therefore, tetrahedral charge plays an important role in controlling the swelling of montmorillonite. The charge origin and variability is recognized as one of the most important features because it influences occupancy of the interlayer space by exchangeable cations (Bergaya et al., 2006b).

Montmorillonite is built up of units loosely held together. Consequently, it expands and cleaves into extremely thin flakes upon agitation in water, giving a huge surface area for a given mass of mineral (Grim, 1939; Tan et al., 2017). In other words, water can enter the interlayer spaces and hydrate interlayer cations. Thus, montmorillonites swell markedly when they get wet, and shrink as they dry (Singer and Munns, 2006). In montmorillonite, most of the counter ions are located between the sheets, with the remainder being at the edges of the flakes (Chiou and Rutherford, 1997; Hendricks et al., 1940), whereas in non-swelling clays the counter ions are sorbed onto the external surfaces only (Li and Gallus, 2005).

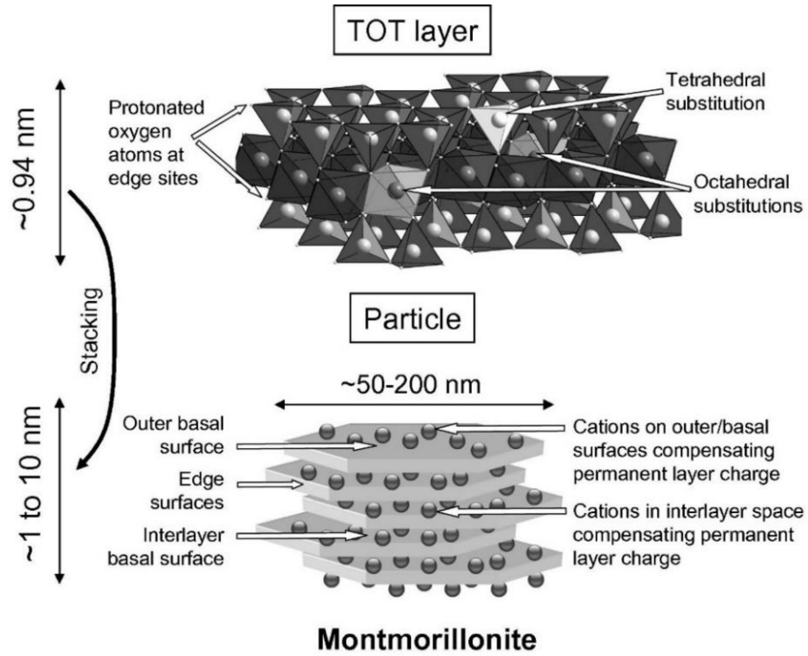

Fig. 2–2 Clay structure of montmorillonite (Tournassat et al., 2011)

Illite is another 2:1 structured clay (Fig. 2–3), which is non-expanding and has a smaller amount of charge than montmorillonite, although they are structurally similar. This is due to the presence of potassium in the interlayer of illite. The interlayer K^+ coordinates perfectly with cavities on the opposing T sheets, locking the layers together (Singer and Munns, 2006). Moreover, the negative charge resulting from isomorphic substitution of Al^{3+} replacing Si^{4+} in the tetrahedral sheet of illite, is predominantly balanced by K^+ (Grim, 1939; Mukherjee, 2013; Powrie, 2013).

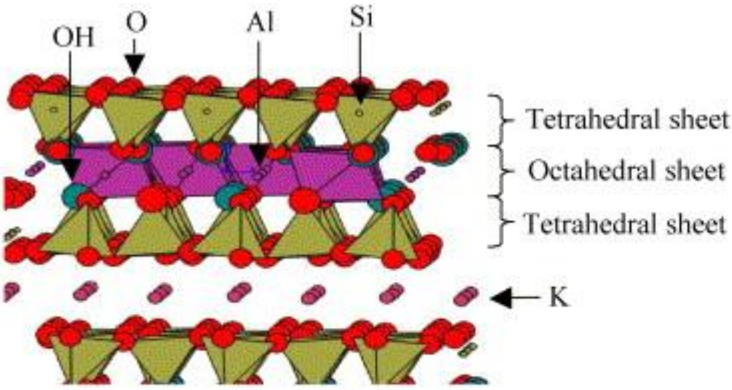

Fig. 2–3 Clay structure of illite (Konan et al., 2007)

The unit layer of kaolin (1:1 clay) is composed of one sheet of tetrahedral silica and one sheet of octahedral alumina (Fig. 2–4). Hydroxyl groups on one unit layer are hydrogen bonded with the oxygen atoms on the adjacent layer, holding the layers together tightly, not permitting water and/or cations to enter the interlayer spaces of kaolinite domains (Singer and Munns, 2006). The composition of the kaolin group minerals is characterized by a predominance of Al^{3+} in octahedral sites, although some isomorphic substitution of Mg^{2+}, Fe^{3+}, and Ti^{4+} for Al^{3+} can occur (Bergaya et al., 2006b; Rengasamy et al., 1975). However, there are only few replacements in the lattice, leading to a low exchange capacity of kaolinite (Ma and Eggleton, 1999; Siefert and Henry, 1947). Additional polar sites, mainly octahedral Al–OH and tetrahedral Si–OH groups, are situated at the broken edges of clay. These sites are conditionally charged, either positive or negative charges depending on the pH, by protonation and deprotonation processes (H^+/OH^- transfer from aqueous phase) (Tombácz and Szekeres, 2006). More details are discussed in Section 2.4.3.

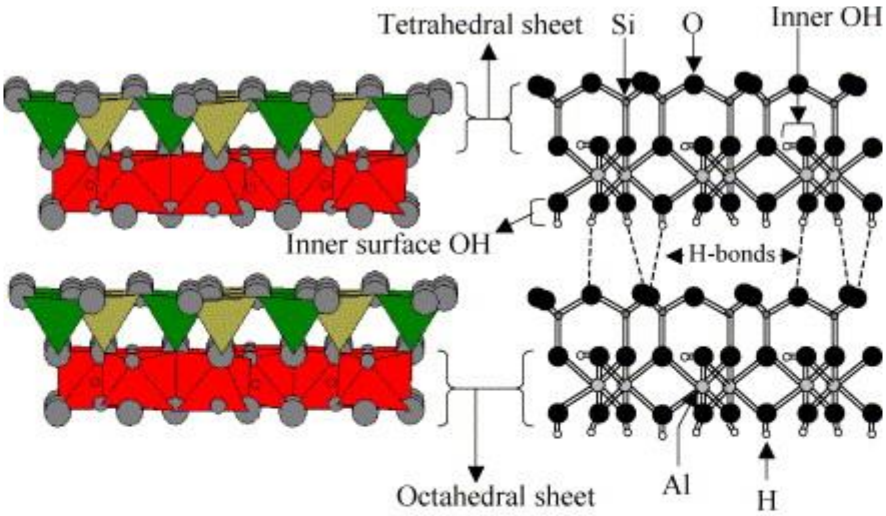

Fig. 2–4 Clay structure of illite (Konan et al., 2007)

The composition and charge vary significantly among montmorillonite, illite and kaolinite clays (Table 2–4). In addition, the thickness and diameter of clay particles vary between and among these clays. The different morphology of the clay minerals has been shown in electron micrographs (Fig. 2–5). As a consequence, the organization in kaolin, illite and montmorillonite clay aggregates is different, as shown in Fig. 2–6. Kaolin has large blocky rigid particles with low width to thickness ratios and has minimal degree of parallel stacking; illite, with width to thickness ratios of less than 10, has some degree of parallel stacking of platy particles; while montmorillonite, with width to thickness ratios exceeding 100, has perfect parallel alignment of thin flexible plates (Oades and Waters, 1991).

Table 2–4 Typical aluminosilicate minerals in the clay fractions of soils (Weil and Brady, 2016)

Mineral	Type	Thickness of cell	Thickness of clay plate	Particle diameter[a]	Surface area External	Surface area Internal	Net negative charge
		nm	nm	μm	10^3 m^2/kg		cmol$_c$/kg
Kaolinite	1:1	0.70	50–2000	0.3–4	5–30		-1 to -15
Montmorillonite	2:1	0.96	1–8	0.01–0.1	80–150	550–650	-80 to -150
Illite	2:1	1.00	>3	0.1–0.3 (or larger)	70–175		-10 to -40

[a] Particle size data from Yong and Warkentin (1975) and Donaldson et al. (1995)

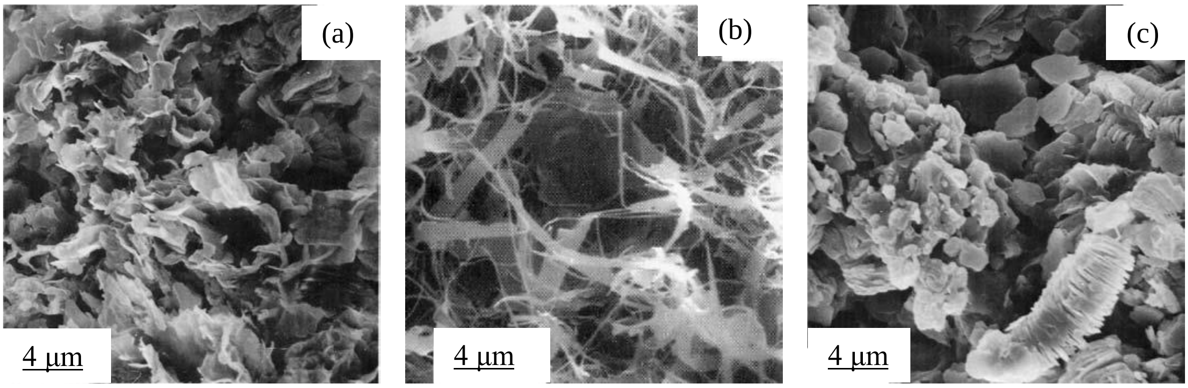

Fig. 2–5 Electron micrographs of clay minerals with varied particle morphology (a) montmorillonite (Lombardi et al., 1987) (b) illite (Lanson et al., 2002) (c) kaolinite (Lombardi et al., 1987)

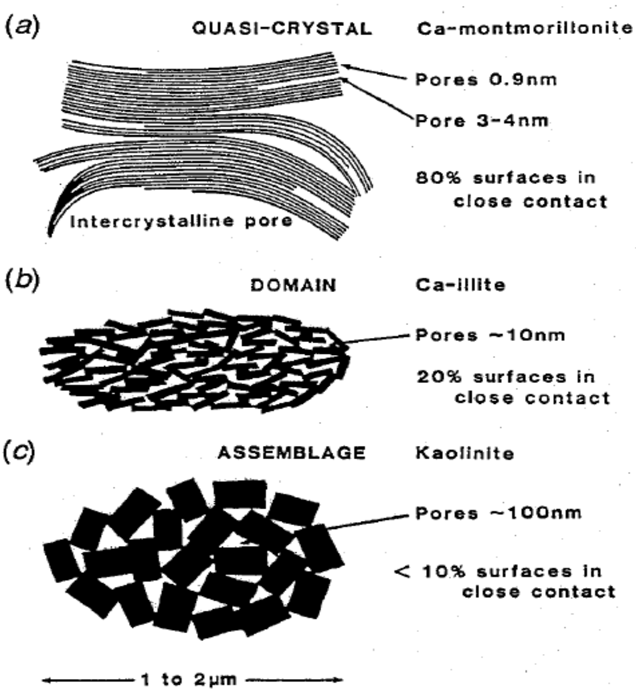

Fig. 2–6 Idealised cross section of clay aggregates: (a) montmorillonite (b) illite and (c) kaolinite (Oades and Waters, 1991)

2.4.1.2. Effect of clay mineralogy on soil structural stability

It has long been recognized that the hydraulic conductivity and aggregate stability of soil is significantly affected by clay mineralogy (Alperovitch et al., 1985; Frenkel et al., 1978; Marchuk et al., 2013a; Ruiz-Vera and Wu, 2006). The hydraulic conductivity of the soil dominant in kaolinite is higher than montmorillonite (assuming equivalent condition) and is less sensitive to variations in solution composition (McNeal and Coleman, 1966). Similar results were produced by Frenkel et al. (1978) where a kaolinitic California soil was less likely to suffer reduction in hydraulic conductivity at low electrolyte concentration than a montmorillonitic soil. Their different behaviours in hydraulic conductivity are likely to be partially related to the common existence of iron and aluminium oxides and hydroxides in kaolinite soils. Fe and Al oxides have been reported to behave as stabilizing agents as there is strong interaction between kaolinite and the (hydro-)oxides of Al and Fe (McNeal et al., 1968). Furthermore, the addition of small amounts of montmorillonite to kaolin soils promotes the dispersion of kaolin flocs. This is due to the adsorption of negatively charged montmorillonite particles on the positively charged kaolin edges, which breakup the edge-to-face particle association of kaolin structure (Schofield and Samson, 1954).

Alperovitch et al. (1985) studied the hydraulic conductivity of clay-sand mixtures and observed more clay dispersion and clay movement for illite than for montmorillonites. Similar results were produced by Oster et al. (1980) whereby dispersibility in illite was much greater than in montmorillonite clay. Red-brown earths (Chromosols), which were dominant in illite, were susceptible to dispersion even at low SAR and under weak mechanical forces (Rengasamy, 1983; Rengasamy et al., 1984). Marchuk et al. (2013a) reported that soil with smectite mineralogy and higher CEC dispersed less than soil dominant in illite and kaolinite at comparable CROSS values. Illites may be more dispersive than smectites because of the differences between the shapes, sizes and/or surface morphologies of the crystals of the two types of minerals (Churchman et al., 1993). Many illites consist of relatively thick particles with little flexibility, irregular surfaces, and can be terraced (Greene et al. 1978). In contrast, smectite particles can be very thin and highly flexible (Emerson 1983). These features mean that the contact between illite particles is less intimate than that between the flexible thin flakes in smectites. This conclusion is in agreement with Oster et al. (1980) who suggested that the high dispersibility of illite was due to a “bad” contact between the terraced planar surfaces of illite and its edges. In contrast, Velasco-Molina et al. (1971) found that at low ESP values, the montmorillonite soil has the highest dispersion as a percentage of total soil clay and the illitic soil sometimes dispersed more than the halloysitic-kaolinitic soil. At high ESP values (>10), the soil clay dispersion was in an order of: montmorillonitic>halloysitic>illite. These results suggest there is a soil specific effect. Other than clay mineralogy, other factors should also be considered in studying the effect of Mg on soil structural stability.

2.4.1.3. Effect of clay particle size on soil structural stability

The size of dispersed clay particles determines the extent of clay migration, the size of pores that can be blocked, and consequently determines the degree of structure degradation (Frenkel et al., 1978; Frenkel et al., 1992; Panayiotopoulos et al., 2004). However, to date, there is limited research on the effect of particle size on soil clay dispersion. Generally, the settling of clay particles in a suspension was following Stoke's law. According to Stoke's law, larger particles settle more quickly than smaller particles. When a particle is falling in a fluid, Stoke's law considers three forces. These include the force of gravity, the force of friction (*i.e.* resistance) and the force due to buoyancy (Lal and Shukla, 2004). However, there are more forces involved in clay colloidal systems, *e.g.* attractive forces from van der Waals forces, repulsive force due to diffused double layer development within clay domains, electrostatic force etc. (more detail is provided in Section 2.5) (Derjaguin, 1941; Leng, 2012; Pashley, 1981; Pashley and Israelachvili, 1984; Quirk, 1994; Verwey and Overbeek, 1948). Kotlyar et al. (1998) studied the flocculation behaviour of ultra-fine aluminosilicate clays and indicated that for particles in the range of 60 to 270 nm, the tendency to flocculate decreased with increased particle size, *i.e.* small particles flocculate more rapidly. The authors stated that this behaviour may result from the low absolute values of the repulsive potential for small particles. Panayiotopoulos et al. (2004) reported that for all of the four soils used (micas and smectites dominant) and for any solution concentration (DI, 5, 10, 50 and 100 mmol/L), SAR (0, 5, 10, 20 and 40) and duration of shaking (30 s or 16 h), the relative dispersion of the coarse clay (1–2 μm) was always greater than the corresponding relative dispersion of the fine clay (<1 μm). Clay dispersion was determined by measuring the optical density at 640 nm of the suspension. Since the coarse and fine clay of any soil used are of similar mineralogy, the authors attributed the higher dispersion of the coarse clay to the size effect only, *i.e.* smaller surface area and lower surface free energy. In addition, the coarse clay fraction displayed higher critical flocculation concentration than the fine clay fraction (Panayiotopoulos et al., 2004).

The particle size may also affect clay dispersion through its effect on ion exchange capability. Decreased clay particle size usually means increased exchange capacity of kaolinite clays (Grim, 1939; Ma and Eggleton, 1999). The exchange capacity of kaolinite increases with decreasing particle size, which would be expected as the exchangeable cations are adsorbed at layer edges and smaller particles result in more edges (Harman and Fraulini, 1940). Similar results reported by Ma and Eggleton (1999) also demonstrate that the CEC values of kaolinite increased as the particle size (mean diameter and thickness) decreased. This is mainly because negative charge originating from isomorphic substitution in kaolinite clay is relatively insignificant, representing only 5% of the total CEC of kaolinite (Ma and Eggleton, 1999). In the case of montmorillonite, the CEC from isomorphic substitution can contribute up to about 80% of the total CEC. Thus, the exchange capacity of montmorillonite does not vary significantly with its particle size since most of the exchangeable cations are located between the layers (Siefert and Henry, 1947; Weil and Brady, 2016).

As discussed in Section 2.4.1.1, particle size differs significantly between kaolinite, illite and montmorillonite. Sides and Barden (1971) studied the microstructure of dispersed and flocculated samples of kaolinite, illite and montmorillonite by adding sodium oxalate ($Na_2C_2O_4$) as a dispersing agent and calcium hydroxide ($Ca(OH)_2$) as a flocculating agent. Their investigation showed that the dispersing and flocculating agents were much more effective in influencing structure of the smaller and colloidally active illite particles than larger kaolinite particles. These larger particles were presumably colloidally inactive and hence relatively inert to the chemical additives. This indicated a system of larger but colloidal inactive particles in the suspended state are more stable. Considering this logically from an aggregated initial state, rather than a suspended one, this would indicate that larger but colloidal inactive particles would be harder to disperse than smaller ones due to the same reasoning.

In summary, changing particle size of a certain clay type may affect the dispersive behaviour through its surface area, CEC (from broken edges) and repulsive forces; the dispersive behaviour among different clay minerals is mainly dependent on its colloidal activity, and particle size to a lesser extent.

2.4.1.4. Effect of clay content on soil structural stability

Clay content can affect soil dispersion to some extent. McIntyre (1979) found highly significant negative correlations between clay content and hydraulic conductivity for 41 illitic soils, but no significant correlation for 7 montmorillonitic soils, from Australia. McNeal and Coleman (1966) found that the hydraulic conductivity of soils with moderate amounts of montmorillonite were more stable than soils high in montmorillonite for seven Western USA soils under low salt and high sodium conditions. Saturated hydraulic conductivity tended to decline more drastically as clay contents increased (Frenkel et al., 1978). These authors stated that high clay content soils had smaller pores and increased tortuosity, which were more susceptible to blockage and volume reduction of conducting pores by dispersed particles and clay swelling. Furthermore, Barzegar et al. (1994) reported that the spontaneously and mechanically dispersible clay was strongly correlated with clay content in 5 soils with varying ESP. Consequently, it is important to examine clay content of each soil when analysing soil dispersive behaviour.

2.4.1.5. Effect of sesquioxides on soil structural stability

Many soils contain sesquioxides, and the interactions between clay and Fe and Al oxides is important in determining the physical and chemical properties of soils, such as soil aggregation, hydraulic conductivity, clay dispersion/flocculation and iron adsorption and exchange (Alperovitch et al., 1985; Arias et al., 1995; Barthès et al., 2008; Beppu and Wada, 1992; Duiker et al., 2003; Goldberg and Glaubig, 1987; Goldberg et al., 1990; Sumner, 1963; Yilmaz et al., 2005). It was generally accepted that the presence of Al and Fe (hydro-)oxides has stabilizing effects on soil structure. The presence of either Fe oxide or Al oxide decreased the critical flocculation concentration relative to that of the clays alone, *i.e.* montmorillonite, kaolinite and montmorillonite/kaolinite mixture (Goldberg and Glaubig, 1987). However, the exact mechanism of the stabilizing effect of Fe or Al oxides remains obscure.

Many factors may influence the effects of Fe or Al oxides on soil structural stability, including pH, clay mineral, the size and content of crystals, the degree of crystallinity, organic matter and the ionic composition of the soil solution (Alperovitch et al., 1985; Arias et al., 1995; Barthès et al., 2008; Duiker et al., 2003; Goldberg, 1989; Goldberg and Glaubig, 1987). Soil stability under high sodium and low ionic strength conditions was largely reduced by partial removal of the free iron oxides, emphasizing the iron oxide content was important (McNeal et al., 1968). Goldberg and Glaubig (1987) reported that the effects of Al and Fe oxides on the critical flocculation concentration of clays was pH dependent, and only when pH was below their zero point of charge, *i.e.* at $pH \approx 9.5$ for Al oxide and at $pH \approx 7.2$ for Fe oxide, did Fe and Al oxides form aggregates with clay particles. Poorly crystalline Fe oxides have larger and more reactive surfaces, which may consequently increase aggregation more than crystalline Fe oxides (Duiker et al., 2003). The ameliorative effect of Al oxides was shown to be greater than that of Fe oxide especially at high pH values, which may be related to the size and morphology of the oxide particles (Goldberg and Glaubig, 1987). Alperovitch et al. (1985) found that the polycations (Fe^{3+} and Al^{3+}) were able to prevent clay swelling, dispersion, and the resultant drop in hydraulic conductivity by cementing clay platelets. The aluminium polycations having planar morphology and higher charge per mole were more effective in reducing the effect of sodium on swelling than the spherical iron polycations. Hence, it is important to pay attention to the interaction between sesquioxides and clays in magnesic soils.

2.4.2. Effect of exchangeable cations on soil structural stability

Usually, Na, K, Mg and Ca are the predominant counter ions in neutral-alkaline soils, constituting the effective CEC as the sum of these four cations. In this section, the effects of Na, K, and Ca on soil structural stability are discussed.

2.4.2.1. Effect of sodium on dispersion

When certain amount of Na is adsorbed on soil particles as exchangeable cations and the concentrations of other soluble ions are low, soils are considered to become sodic. Two indices, exchangeable sodium percentage (ESP, Eq. 2.5) and sodium adsorption ratio (SAR, Eq. 2.6), are commonly used to assess soil sodicity and structural stability. ESP is the amount of exchangeable Na (cmol_c/kg) expressed as a proportion of effective cation exchange capacity (CEC_{eff}):

$$ESP = \frac{[Na^+]}{[Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+]} \times 100 \qquad \text{(Eq. 2.5)}$$

In Equation 2.5, concentrations of Na, K, Ca and Mg are expressed in cmol_c/kg (Qadir and Schubert, 2002; Sumner, 1993; US Salinity Laboratory Staff, 1954). When dealing with an irrigation water or a soil solution, SAR is the index used to define the sodicity (Bower and Hatcher, 1962; Sumner, 1993). SAR involves concentrations of Na, Ca and Mg in a soil solution with an indication of the effect of Na on the soil structure, whereby increasing SAR results in increasing sodicity:

$$SAR = \frac{[Na^+]}{(0.5[Ca^{2+}] + 0.5[Mg^{2+}])^{1/2}} \qquad \text{(Eq. 2.6)}$$

In Equation 2.6, the concentrations of Na, Ca and Mg in solution are in mmol of charge per litre (US Salinity Laboratory Staff, 1954).

An alternative index is the exchangeable sodium content (ESC), in which levels of sodium are expressed on an oven-dried soil basis rather than relative to the cation exchange capacity. Cook and Muller (1997) compared the abilities of ESP and ESC to explain variation in soil structural stability across soil types using data from 15 published data sets, and concluded that ESC is generally a better index of soil sodium levels than ESP and should be used more widely.

In Australia, soils with an ESP greater than 5 (McIntyre, 1979) or 6 (Northcote and Skene, 1972) is considered to be sodic. In comparison, sodic soil is specified to have an ESP greater than 15 in U.S. (US Salinity Laboratory Staff, 1954). Northcote and Skene (1972) attributed the lower threshold value of ESP for sodicity in Australian soils to the very low contents of soluble minerals, especially Ca, which are necessary to maintain the electrolyte concentration during leaching. In fact, the difference between the threshold values is related to different water used in hydraulic conductivity experiments. McIntyre (1979) used water with electrolyte concentration of 0.7 $mmol_c/L$ in the measurement of the hydraulic conductivity of 71 Australian soils and proposed the ESP value of 5 to define the boundary between sodic and non-sodic soils. By comparison, in the U.S. Salinity Laboratory, tap water with an electrolyte concentration of 5–10 $mmol_c/L$ was used to measure the hydraulic conductivity of disturbed soil, thereby leading to an ESP value of 15 for designation of sodic soil (Quirk, 2001; Shainberg and Letey, 1984; Shainberg et al., 1981). The relationship between ESP and SAR has been studied with numerous soil samples. The ESP value of a red-brown earth soil is approximately twice the SAR of a 1:5 soil to water extract (Rengasamy et al., 1984). In the 1:5 soil water extract, soil dispersed spontaneously when SAR>3, where SAR of 3 is the critical value of sodic soil (equivalent to ESP of 6) according to Rengasamy and Olsson (1991). However, in a study of Songnen Plain soils, a different regression model of ESP and SAR was proposed by Chi et al. (2011), as well as for many other soils and investigations throughout the years (Table 2–5). This indicates that the ESP-SAR relationship is not constant, and likely varies due to different clay minerals, ionic strength, clay content, organic matter and other factors (Endo et al., 2002; Kopittke et al., 2006; Nelson and Oades, 1998; Qadir and Schubert, 2002).

High ESP or SAR values (*i.e.* sodic soil or irrigation with high SAR water) can cause the dispersion of aggregates, limitation of water and gas transport, reduction of hydraulic conductivity, degradation of soil structure and hence productivity (Rengasamy and Olsson, 1993; So and Aylmore, 1993). In a mixed Na-Ca montmorillonite system (Fig. 2–7), the charges within tactoids are neutralized mainly by Ca, while the outer surfaces of clay tactoids are enriched in Na (Shainberg and Letey, 1984; Sumner, 1993). The outer surface of montmorillonite clay, where Na dominates, can further separate into single platelets. The introduction of Na (up to 15%) into Ca-saturated smectic system has little effect on swelling (Bar On et al., 1970). However, this small addition of Na has a profound effect when considering the electrophoretic mobility of clays (Bar On et al., 1970; Sumner, 1993). In terms of soil management, replacement of Na from cation exchange sites with Ca can thereby ameliorate high Na and its adverse effects (Bennett et al., 2014a; Bennett et al., 2015; Bennett et al., 2014b; Bennett et al., 2016b; Bronick and Lal, 2005).

Table 2–5 ESP-SAR relationships for various soils

Soils	Relationship between ESP and SAR	R^2	Reference
59 soil samples, Western U.S.A.	$ESP = \frac{100(-0.0126 + 0.01475SAR)}{1 + (-0.0126 + 0.01475SAR)}$	0.85	US Salinity Laboratory Staff (1954)
35 soil samples, A horizon, Canada	$ESP = \frac{100(0.0076 + 0.0058SAR)}{1 + (0.0076 + 0.0058SAR)}$	0.90	Harron et al. (1983)
35 soil samples, B horizon, Canada	$ESP = \frac{100(-0.0180 + 0.0173SAR)}{1 + (-0.0180 + 0.0173SAR)}$	0.90	Harron et al. (1983)
138 red-brown earth, Australia	$ESP = 1.95SAR^* + 1.8$	0.82	Rengasamy et al. (1984)
117 samples, Northeast China	$ESP = 10.72\ln(SAR) - 15.36$	0.88	Chi et al. (2011)
117 samples, Northeast China	$ESP = 11.44\ln(SAR^*) + 5.48$	0.76	Chi et al. (2011)

*SAR is measured in the 1:5 extract.

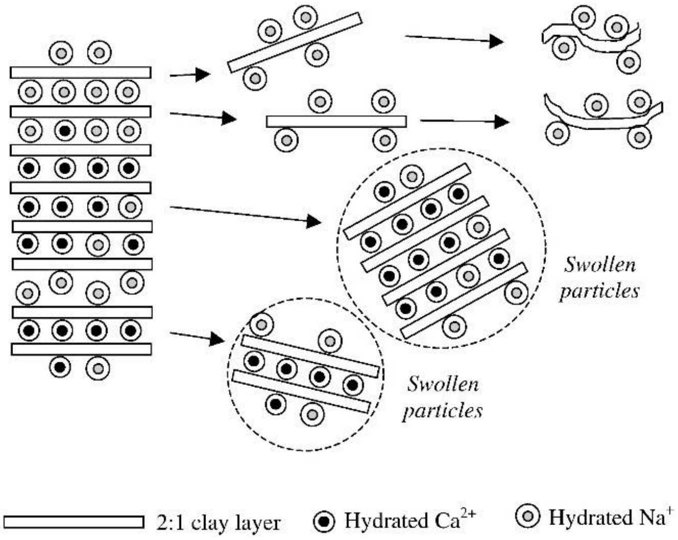

Fig.2–7 Comparison of particle arrangements in a homoionic Na montmorillonite with that in a Na-Ca system (Tan et al., 2017)

2.4.2.2. *Effect of potassium on dispersion*

Traditionally, application of potassium (K) to soils has been perceived as beneficial for soil fertility and crop yield as K is a major nutritional element for plants (Fageria, 2008). However, while there are potential negative effects of K on soil structural stability, the extent and occurrence of this was initially ambiguous given that different studies revealed stabilizing effects as well as destabilizing effects of K (Holthusen et al., 2012). Increasing the exchangeable potassium percentage (EPP) from 1.5 to 13 did not increase clay dispersion of a sandy loam soil, and a decreasing dispersed clay amount from a clay soil was observed when EPP increased from 2 to 10.5 at the expense of exchangeable Na and Ca (Levy and Torrento, 1995). Moreover, EPP increasing from 0 to 20 improved hydraulic conductivity for a loamy sand and heavy clay soil, though had a negative effect on a light clay soil, which was richer in illite (Chen et al., 1983). In contrast, negative effects of K on hydraulic conductivity have been reported (Levy and Van Der Watt, 1990; Quirk and Schofield, 1955). Similar findings were reported by Arienzo et al. (2012) whereby hydraulic conductivity of a smectite-rich soil decreased after percolating potassium adsorption ratio (PAR) solutions (values of 20 and 40), although the decrease was less than for the corresponding SAR solutions. Recent studies have confirmed that K can also cause soil clay dispersion (Bennett et al., 2016a; Marchuk et al., 2013a; Marchuk and Marchuk, 2018; Rengasamy and Marchuk, 2011; Smiles and Smith, 2004). Rengasamy and Sumner (1998), in their study of the critical flocculation concentration of homoionic soil clays, found that K is not equivalent to Na in causing clay dispersion in soils. Further, based on the calculation of flocculation power (detailed in section 2.3.2), K has been found 0.56 as effective in causing dispersion as compared to Na, when the degree of Na causing dispersion was considered as 1. This coefficient (0.56) has been applied in the concept of CROSS and EDP (detailed in section 2.3.2) – new indices to assess soil structural stability (Bennett et al., 2016a; Rengasamy and Marchuk, 2011). Furthermore, Dang et al. (2018b) demonstrated for four soils of ranging mineralogy that applying a concentration of K, based on generalised coefficients (Rengasamy and Sumner, 1998) of equivalence to Na effect, did not result in similar reduction in K_{sat} between the K and Na equivalent solutions. Indeed, where the solution concentration increased, the K appeared to make the soil more resilient to expected adverse K concentrations. Marchuk et al. (2016) suggested that illitisation of minerals may be responsible, but could not confirm this. The conflicting results reported may be attributed to differences in clay mineralogy (Arienzo et al., 2012; Levy and Torrento, 1995; Shainberg and Levy, 1992), K fixation removing K from solution (Holthusen et al., 2012), or in offsetting adverse Na effects where Na is exchanged for K thereby potentially improving soil structure. This all suggests that the critical flocculation concentration (CFC) used for K is indeed soil specific, as stated by Smith et al. (2015), where CFC is defined as a minimum electrolyte concentration required to develop a clear supernatant for a dispersed soil or clay suspension in a given time.

2.4.2.3. Effect of calcium on dispersion

Ca is often considered as a beneficial ion, which prevents structural deterioration of soil. Gypsum ($CaSO_4 \cdot 2H_2O$) is reported as the most widely used source of calcium for sodic soils in Australia (Ali et al., 2018; Bennett et al., 2014a; Bennett et al., 2015; Bennett et al., 2014b; Bennett et al., 2016b; McKenzie et al., 1993).

Ca can inhibit clay dispersion and the associated disruption of aggregates by replacing Na, K and Mg in clay and aggregates (Armstrong and Tanton, 1992; Sumner, 1993), where the thickness of diffuse double layer in Ca system is thinner. Additionally, Ca improves soil structure through cationic bridging between clay particles and soil organic matter (Bronick and Lal, 2005).

Cations differ in the strength with which they are adsorbed in soils, which has a major influence on the reclamation of salt-affected soil. The cation selectivity coefficients are related to cation valency and hydrated radius. When in contact with water, the cations will form a solute hydration shell. The larger the dehydrated ion is, the less hydrated it is, as indicated in Table 2–6. Dehydrated K (0.133 nm) is larger than dehydrated Na (0.098 nm), but hydrated K (0.532) is smaller than hydrated Na (7.9 Å). Similarly, Mg is a small ion with a valence of 2 but has a large hydration shell than hydrated Ca (divalent cation).

Table 2–6 Ionic radii and valency for different cations (Evangelou and Phillips, 2005)

Ion	Ionic radii (nm)	
	Not hydrated	Hydrated
Na^+	0.098	0.790
K^+	0.133	0.532
Mg^{2+}	0.089	0.108
Ca^{2+}	0.117	0.960

The strength with which cations are adsorbed in soils is as follows, due to the effects of valence and hydrated radius (Sparks, 2003):

$$Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ = NH_4^+ > Na^+$$

From this Lyotropic series, it is noted that valence dominates strength of adsorption, but if two cations have the same valence, the ion with the smaller hydrated radius is usually preferred.

2.4.3. Effect of pH on soil structural stability

A pH value measures the negative logarithm of the hydrogen ion concentration in a solution (Weil and Brady, 2016). An acidic soil usually refers to soil with a pH less than 6.5, while soils possessing pH values greater than 7.4 are categorised as alkaline. Soils with pH of 6.6–7.3 are considered to be in the neutral range (Hazelton and Murphy, 2007; Rengasamy and Olsson, 1991). Neutral soil is free of trivalent exchangeable Al^{3+} and free of manganese toxicity, and has the majority of nutrients available, which generally indicates optimum soil conditions for crop growth (Chesworth, 2008). Most soils have a pH in the range of 4 to 9.

pH has been found to affect dispersive behaviour in pure clay minerals (Chorom and Rengasamy, 1995) and in soils (Chorom et al., 1994; Marchuk et al., 2013a). At constant SAR and electrolyte levels, clay dispersion increased with pH for two arid-zone soils (Suarez et al., 1984). Similar results were observed for a Na dominant suspension whereby adding a small amount of NaOH redispersed a partially flocculated sodium-saturated kaolinite in distilled water with initial pH≈4 (Schofield and Samson, 1954). The CFC values of three arid-zone soils increased with increasing pH from 5.5 to 9.5 (Goldberg and Forster, 1990), suggesting that a more acidic solution resulted in easier flocculation. These results support Frenkel et al. (1978) who found the hydraulic conductivity of a nonacidic kaolinitic soil to be significantly less within an exchangeable Na dominant environment than for an acidic kaolinitic soil under the same conditions.

The effect of changing pH on dispersive behaviour relates to the changes in net charge on soil clay particles (Chorom et al., 1994). When the net total particle charge in a soil is zero, the pH value is called the point of zero charge (PZC). In most cases, if the pH of a soil is above its PZC, the soil surface will have a net negative charge and predominantly exhibit an ability to attract cations. Conversely, soil with pH values below the PZC will mainly retain anions (Appel et al., 2003). When the soil pH reaches the PZC, clay dispersion will not occur; that is, in a dispersed suspension, altering the pH to the value of the PZC will lead to flocculation irrespective of the solute suite (Rengasamy and Olsson, 1991).

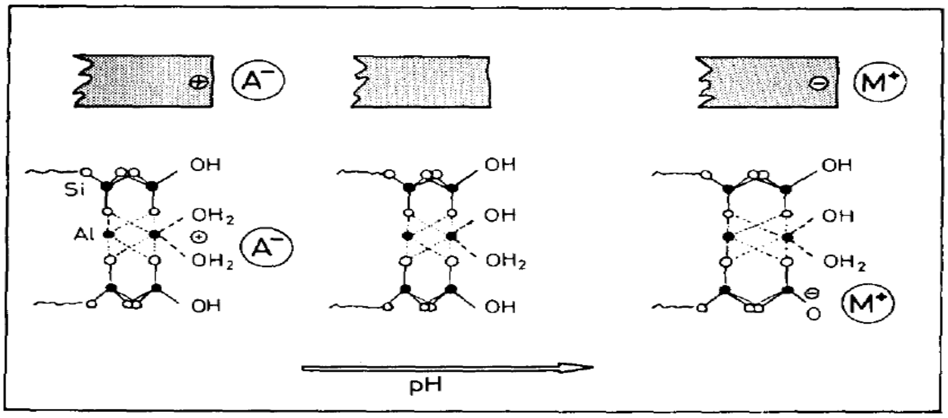

Fig. 2–8 Variable charge density on the crystal edges of 2:1 clay minerals as pH increase: desorption of protons and ionization of silanol groups impart an increasing negative charge density to the edges (Lagaly, 1989).

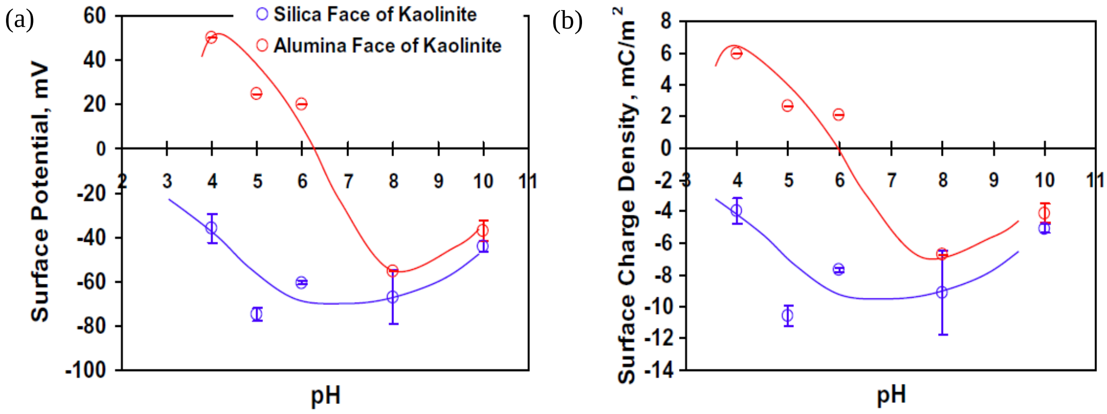

Fig. 2–9 Surface potential (a) and surface charge density (b) of the silica face and the alumina face of kaolinite particles as a function of pH (Gupta and Miller, 2010).

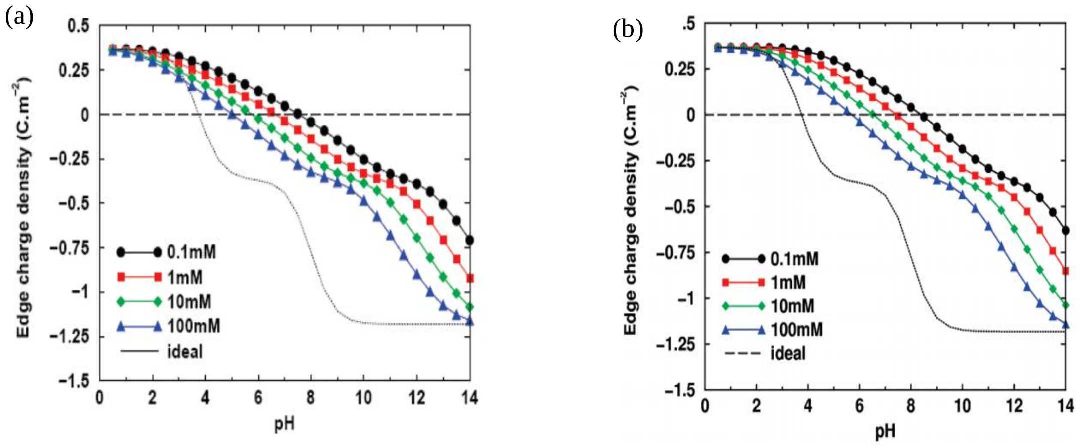

Fig. 2–10 Simulated edge charge density for (a) montmorillonite (basal charge -0.7 e/nm^2) and (b) illite (basal charge -1.2 e/nm^2) (Delhorme et al., 2010).

Depending on clay mineralogy and oxide contents, soils may exhibit a net negative or positive charge at high or low pH conditions (Chorom et al., 1994). For example, iron and aluminium oxides generally undergo a surface charge reversal around pH=7–9, where they are positively charged below that pH and negatively charged above (Suarez et al., 1984). Most Australian soils have pH-dependent charge. The sign of charge (+ or –) at mineral edges changing with pH is shown in Fig. 2–8. The edges of kaolinite are known to become positively charged at a low pH (<4.5) and negatively charged at a high pH (Mukherjee, 2013; Schofield and Samson, 1954). Furthermore, the silica face of kaolinite was found to be negatively charged at pH>4, whereas the alumina face surface was positively charged at pH<6 and negatively charged at pH>8 (Fig. 2–9) (Gupta and Miller, 2010). Research has indicated that the aggregation size of kaolinite in 0.01 M NaCl solution is a function of pH, while the average particle size of montmorillonite is almost constant (Tombácz and Szekeres, 2006). This can be related to the fact that montmorillonite clays are generally considered to have a permanent charge that does not vary with pH. However, study has shown that the edge of montmorillonite and illite minerals also carry pH-dependent charge (Delhorme et al., 2010) as shown in Fig. 2–10. On the basis of these finding, further investigation into the clay dispersive behaviour in a range of pH values is required in terms of contrasting clay minerals saturated with different type of exchangeable cations, particularly Mg and K.

2.4.4. Effect of electrolyte concentration on soil structural stability

Many authors have reported the effects of electrolyte concentration on soil clay dispersion, where electrolyte concentration is directly proportional to electrical conductivity (Agassi et al., 1981; Arora and Coleman, 1979; Dang et al., 2018d; Ezlit et al., 2013; Quirk, 2001; Rengasamy et al., 1984). The classical work in this space is attributed to Quirk and Schofield (1955), who noted that decreasing the electrolyte concentration of the irrigation water used to irrigate fields that had previously received high concentration and marginal irrigation water containing Na, resulted in dispersion and surface sealing. This subsequently led them to define the threshold electrolyte concentration (C_{TH}) and threshold turbidity concentration (C_{TU}). The C_{TH} defines a measureable departure from a Ca dominant stable state, whereby this departure (usually minimise the reduction in K_{sat} within tolerable limits) is defined as a reduction in K_{sat}. The C_{TU} is the point where turbidity is first observed in a leachate, or the aggregation-dispersion boundary condition (Dang et al., 2018c). CFC, which is the minimum electrolyte concentration required to develop a clear supernatant for a dispersed soil or clay suspension in a given time

(Quirk, 2001; Shainberg and Letey, 1984), differs from the C_{TU} on the basis of a difference in energy required to disperse an aggregated system as opposed to flocculate a dispersed one; increasing the electrolyte concentration beyond the CFC, flocculates the soil.

While the CFC does not directly pertain to an aggregated system, it has been used to determine equivalent effects of ions on soil stability, and provide a valuable means by which to predict soil stability. The CFC is strongly dependent on the nature of ions introduced. Even with the same valence, the flocculating power of different cations differs (Rengasamy and Sumner, 1998). However, CFC is also related to the presence of surface coatings or other impurities, degree of hydroxyl Al or Fe-polymerization, pH, tactoid formation, thixotropy and the mutual flocculation of positive edge faces and negative surfaces (Arora and Coleman, 1979; Jia et al., 2013; Shainberg and Letey, 1984). Hence, there is further value in assessing the extent of CFC variation, especially with regard to Mg.

Based on the work of Quirk and Schofield (1955) it is well established that soil permeability can be conserved by maintaining an electrolyte concentration that is equivalent to, or greater than, the C_{TH}. However, it is further established that both the C_{TH} (Bennett and Raine, 2012; Dang et al., 2018d; Marchuk and Rengasamy, 2012) and the C_{TU} (Dang et al., 2018c) are soil specific, and likely to be affected by the flocculating power of the ionic suite, amongst other factors. When the electrolyte concentration is below C_{TH}, adverse effects equivalent to those discussed around sodicity (Section 2.3.1) are evident (Rengasamy and Olsson, 1991). Quirk (2001) states that the flocculation concentration is almost twice that of the threshold concentration, illustrating that application of either the threshold concentration or flocculation concentration is related to the practical irrigation problem. Quirk (2001) stated that with border-check irrigation on Riverina clay soil the threshold concentration is appropriate. Conversely, if the application of an irrigation water is more aggressive, (*i.e.* large flow rates in furrows which would disrupt clay domains to some extent), the flocculation concentration may be more appropriate in order to prevent the formation of surface seals (Quirk, 2001). Smith et al. (2015) subsequently used C_{TH} data instead of CFC values in optimising CROSS and reported different coefficients for K and Mg from Rengasamy and Sumner (1998).

Recently, de Menezes et al. (2014) argued that it is not suitable to use an arbitrary percent reduction in hydraulic conductivity to specify or guide soil irrigation in practice. Instead, the authors suggested applying a minimum acceptable infiltration rate of water rather than a percent reduction in hydraulic conductivity. Bennett and Raine (2012) and Dang et al. (2018c) questioned the C_{TH} curves in Figure 4.2.2 (Fig. 2–11) of the ANZECC guidelines (2000) as an appropriate means for the selection of saline-sodic water to maintain soil permeability, on a similar basis to that of de Menezes et al. (2014) and due to the soil specificity of both the C_{TH} and C_{TU}. Using high SAR water with a suitable C_{TH} can maintain soil permeability, but long term irrigation with high electrolyte solutions may cause accumulation of water-soluble salts in the soil if a leaching fraction is not employed. Additionally, where rainfall interacts with the soil solution, a buffering system for the solution electrolyte might be needed (Ali et al., 2018; Bennett et al., 2016b). Dilution of the soil solution is linear, while dilution of the exchangeable cation suite is nonlinear, meaning that in dynamic systems the rate of dilution also needs to be considered, and may actually protect the soil without requirement for buffering (Ali et al., 2018). On this basis, the EC has a rather significant effect on the dynamics of soil structural stability and is therefore considered to be a key factor.

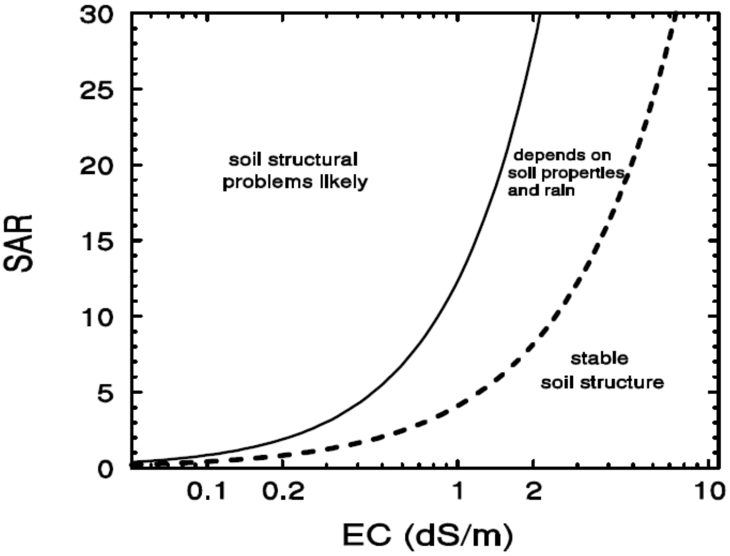

Fig. 2–11 Relationship between SAR and EC of irrigation water for prediction of soil structural stability (Figure 4.2.2 in ANZECC guidelines (2000) which was modified from DNR (1997)). Water quality that falls to the right of the dashed line is unlikely to cause soil structural problems. Water quality that falls to the left of the solid line is likely to induce degradation of soil structure; corrective management will be required (e.g. application of lime or gypsum). Water that falls between the lines is of marginal quality and should be treated with caution.

2.4.5. Effect of organic matter on soil structural stability

Organic matter (OM), which often ranges from 1 to 6% of total topsoil mass, is documented as having a highly heterogeneous composition (Churchman et al., 1993). Organic matter contributes to the CEC of soils, augmenting the clay fraction. The CEC of soil OM ranges from

60 to 300 cmol$_c$/kg, which is generally much greater than the absolute charge of clay minerals. Tisdall and Oades (1982) provided an idealized model which demonstrated that an aggregate of soil is built up of structural units of various sizes held together by OM and other binding agents acting on a range of different scales depending on the type of OM (Fig. 2–12). In particles <2 μm diameter, organic material is likely to be sorbed onto the surface of clays and held firmly by the various bonds. This interaction may increase or decrease the attraction between the particles depending on the nature of OM.

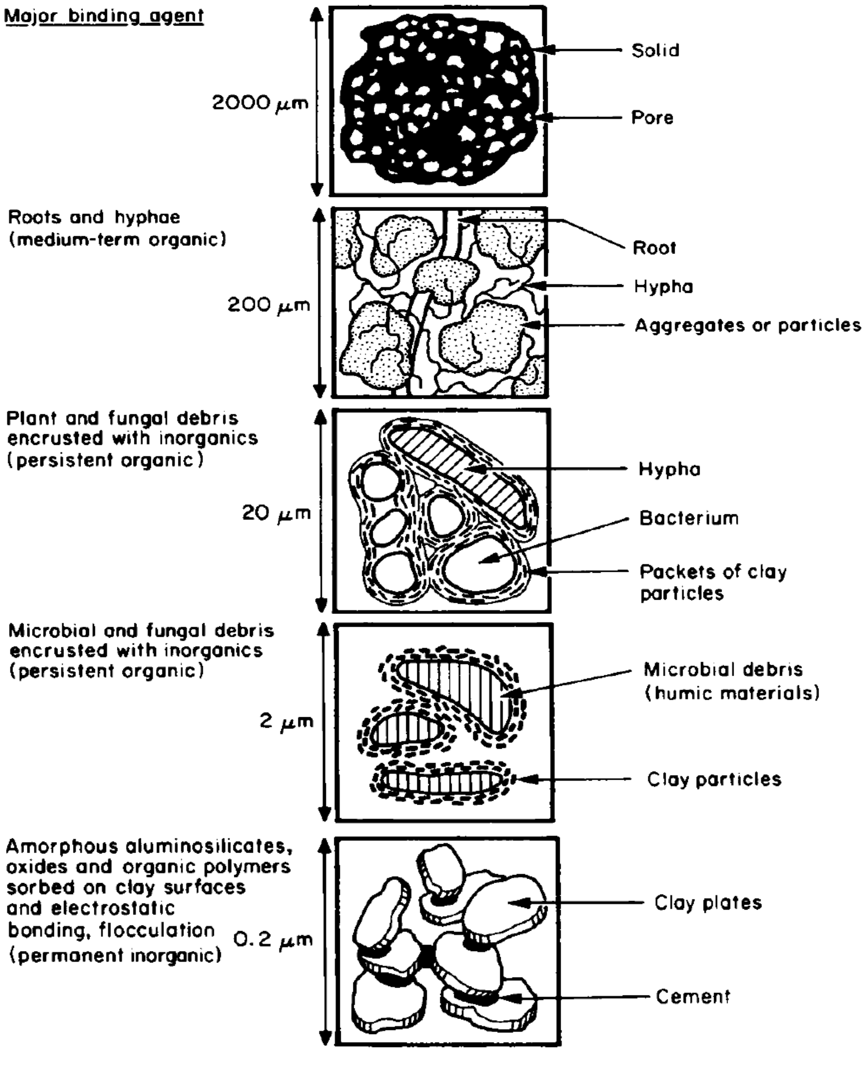

Fig.2–12 Model of aggregate organization with major binding agents indicated. (Tisdall and Oades, 1982)

Many studies have been conducted on the effects of OM on aggregate stability, soil hydraulic conductivity and soil clay dispersibility (Furukawa et al., 2009; Lado et al., 2004; Tisdall and Oades, 1982). Organic matter may enhance or prevent soil dispersion depending on the nature of the OM (Murphy, 2015; Nelson et al., 1999). A large proportion of amino acid or protein material has been found associated with easily dispersed clay, which suggests OM in this form may enhance dispersion of clays through increasing the negative charge of clay particles or complexing Ca^{2+} and other polyvalent cations (Nelson and Oades, 1998). On the other hand, other organic materials such as polysaccharides, roots and fungal hyphae bind microaggregates into stable macroaggregates (Six et al., 2000b). The OM content has been found to be one of the main factors controlling the aggregate stability of soils. An increase of OM content from 2.3 to 3.5% reduced aggregate breakdown and soil dispersibility (Lado et al., 2004). Moreover, the influence of OM varied with its quantity and the clay content; the more organic matter there was, the more stable the soil became, particularly in soil containing little clay (Wuddivira and Camps‐Roach, 2007).

Goldberg et al. (1990) found that adding dissolved organic matter enhances clay dispersion. The authors discussed that the positive effect of organic matter on soil structure probably occurs through binding of soil particles by roots and hyphae at the aggregate level, but at the clay-particle level the negative charge of organic anions enhances clay dispersion. Marchuk et al. (2013a) found that dissolved organic matter led to increased clay dispersion in soils dominant with monovalent ions. They concluded that the role of organic matter in clay dispersion appeared to be in altering the negative charge available for water interactions, whereby a reduction of negative charge resulted in a reduction in clay dispersion. Additionally, Durgin and Chaney (1984) studied the effect of dissolved organic matter from *Douglas-fir* roots on the dispersion of kaolinite and suggested that the size of the organic anion may determine its influence. If the organic anion size is shorter than the clay edge, its specific adsorption offsets the positive charge at the adsorption site. This increases negative charge to the particle, and hence, produces dispersion. Alternatively, if the organic anion is longer than the clay edge it will attach to the edges of several clay particles and bind them together, preventing dispersion. Furthermore, Nelson et al. (1999) concluded that the dispersibility of clay fractions was a function of the amount and type of organic matter, selectivity of cations and their particle size.

In terms of the interactions between different cations and organic matter and their effect on structural stability, it is generally believed that Ca improves soil structural stability through cationic bridging with clay particles and soil organic matter, while Na has direct chemical and physical effects on soil organic matter, consequently causes increased solubility of organic matter as compared to Ca by up to several orders of magnitude (Churchman et al., 1993; Nelson et al., 1999; Nelson and Oades, 1998). However, there is a scarcity of literature concerning the interaction between Mg and organic matter in terms of soil structural stability. Therefore, investigation into the interaction of Mg with soil organic matter is critical in driving our understanding of soil structural dynamic.

2.4.6. Effect of Mechanical stresses on soil structural stability

When soil aggregates are subject to mechanical stress, clay dispersion may occur at low levels of sodicity and low electrolyte concentration in soil that was previously structurally stable (Chorom et al., 1994; Curtin et al., 1994a). Mechanical stress includes rain droplet impact, cultivation, trampling by animals and any intervention where a stress state distribution is applied to a soil. To simulate similar levels of mechanical processes occurring in agriculture and in the environment, external force has been applied when examining soil structural stability in the laboratory. Rengasamy et al. (1984) proposed a set of measurements of clay dispersion called ‘spontaneous dispersion’ and ‘mechanical dispersion’ tests to simulate minimal disturbance and intense energy input (*e.g.* wet soils under tillage operations or rainfall impact). The authors derived the threshold lines relating to SAR and electrolyte concentration for spontaneous and mechanical dispersion based on Red Chromosols and Sodosols, classifying dispersive soils as spontaneously or potentially mechanically dispersive (only dispersed with applied stress) (Rengasamy et al., 1984). These approaches have led to methods that assess water dispersible clay both in terms of spontaneous and mechanically dispersive energies (Amézketa and Aragüés, 1995b; Czyż and Dexter, 2015; Rengasamy et al., 1984; Yousaf et al., 1987a). The data from this work demonstrated the amount of clay dispersed in a suspension from a given amount of soil can provide a useful measure for predictive analyses. While use of a turbidimeter to measure the turbidity of a suspension provides a rapid means to quantify dispersion, there is no rapid means to convert the practically meaningless turbidity units into grams per litre of dispersed clay for quantitative use. Such a method would be highly useful in future soil stability experimentation in terms of collecting large data sets that will facilitate the development of more complex models.

2.5. Theories regarding the clay-colloidal system

It is extremely important to understand the forces involved in the clay colloidal system, as these forces between charged particles in an aqueous electrolyte solution determine clay flocculation and dispersion behaviour (Boström et al., 2001). When soil interacts with water, clay particles can separate from the aggregates to form a dispersed colloidal suspension depending on the balance between repulsive and attractive forces among the suspended particles (Quirk, 2001; Shainberg and Levy, 2005; Sumner, 1993). When attractive forces overcome the repulsive forces, the separated clay particles could amass together and settle. This is termed flocculation (Quirk, 2001; Sumner, 1993). It is often believed that the repulsive force is due to the development of a diffuse double layer, and that the attractive forces comes from van der Waals forces; *i.e.* the Derjaguin, Landau, Verwey and Overbeek (DLVO) theory. However, DLVO theory has had limited success in describing the surface and interparticle forces controlling colloidal behaviour. To date, it has only been used to make reasonable predictions for free swelling clay systems, notably Na and Li montmorillonites (McBride, 1997; Quirk and Marcelja, 1997). It cannot explain the limited swelling phenomenon of Ca montmorillonite over a very wide range of $CaCl_2$ concentration (Kjellander et al., 1988; Quirk et al., 1986). This led these authors to refer to the Ca dominant system as a potential minima, or potential well, where changes in energy (osmotic potential) did not induce changes in clay platelet separation. The reporting of short range hydration force and the different effect of ions on clay swelling and dispersion lead more researchers to pay attention to specific ion effects, which are beyond DLVO theory. Recently, Marchuk and Rengasamy (2011) introduced the ionicity concept stating that the clay–cation bond is a mixture of covalent and ionic bond (electrostatics). In order to understand the force interactions in clay colloidal systems, these three theories including DLVO theory, specific ion effects, and ionicity concept are presented and discussed in this section.

2.5.1. Derjaguin, Landau, Verwey and Overbeek theory

The DLVO theory of colloid stability has served since the 1940s, and states that dispersion or flocculation depends on the net effect of attraction of van der Waals forces and repulsion of electrical double layer forces (Derjaguin, 1941; Verwey and Overbeek, 1948). If the former dominates, two clay particles or surfaces would come together and adhere as flocs, whereas when the latter dominates they would be repelled as a dispersion (Israelachvili and McGuiggan, 1988; Lal and Shukla, 2004; Sides and Barden, 1971).

2.5.1.1. Repulsive force: diffuse double layer and zeta potential

The surface of clay particles is often negative charged mainly due to isomorphic substitution (Section 2.4.1). The clay electrostatic potential is therefore negative with respect to the bulk solution. The region with negative electrostatic potential accumulates an excess of cations attracted by the Coulomb forces, and repels negative ions of the electrolytes in the soil solution and/or negative charged clay particles (Fig. 2–13). The negative charge on the clay surface and positive charge of the balancing cations create an electrical double layer around the clay particle. The excess of cations gradually lowers the electrostatic potential to zero in the bulk electrolyte. Different models have been proposed to describe the distribution of ions, potential and charge. The most used is the Stern model, as shown in Fig. 2–13, which comprises a single ion thick layer fixed to the clay surface (Helmholtz model) and a diffuse layer joining with the bulk solution (Gouy–Chapman model) (Lal and Shukla, 2004; Stojek, 2010). A Stern layer is approximately two water monolayers thick (0.55 nm) in which there is a rapid fall in potential to the value at the Gouy plane; the behaviour of ions in the diffuse part of the double layer is governed by the Gouy potential. The total surface charge is balanced by counterions in the Stern layer and by the excess of counterions over coions in the Gouy layer (Quirk, 1994).

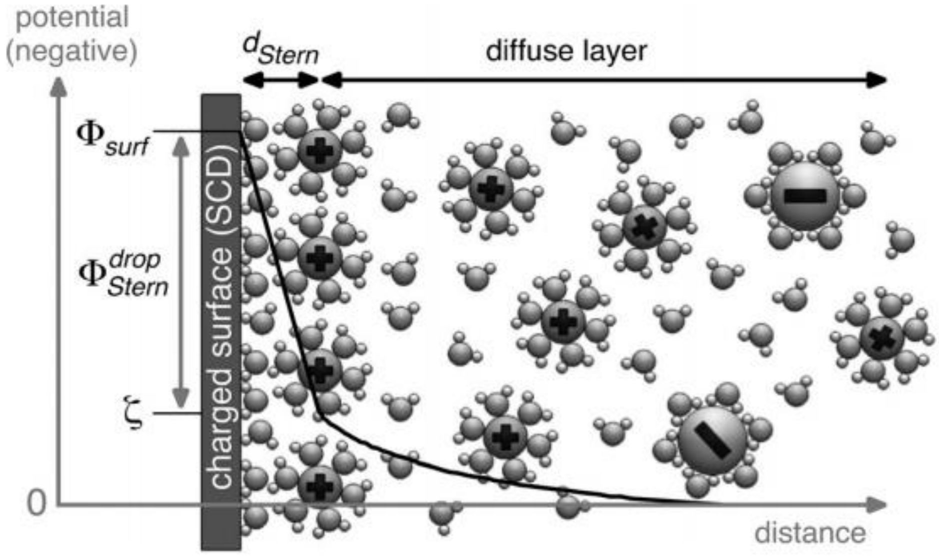

Fig. 2–13 Stern model of the electrical double layer showing the distribution of hydrated cations, coions and water molecules; the potential profile of the Stern and diffuse layers is a function of distance from the charged clay surface (solid line) (Brown et al., 2016).

As shown in Fig. 2–13, the potential difference between the fixed (Stern layer) and freely mobile diffuse layer (shear plane) is defined as the zeta potential (ζ-potential). However, the determination of ζ-potential is often indirect, and is obtained from the electrophoretic mobility (EM, velocity per unit electric field) of particles by the Smoluchowski equation (Aydin et al., 2004). Measurement of the ζ-potential of clays gives a measure of the net charge on a clay particle (Marchuk and Rengasamy, 2011), which differs from the cation exchange capacity.

The ζ-potential is important in assessing the tendency for soil colloids to disperse (Aydin et al., 2004). This was demonstrated by Marchuk et al. (2013a) who used four soils with different clay mineralogy and organic carbon, showing that clay dispersion depended on net charge (ζ-potential) of the dispersed clays, rather than the charge attributed to the clay mineralogy and/or organic matter (*i.e.* CEC). Generally, when the ζ-potential is higher than +30 mV or lower than -30 mV, colloidal (clay dispersion) systems are considered to be stable, meaning that the dispersed clay does not flocculate.

The ζ-potential (or EM) of a particle depends on surface charge density, electrolyte concentration, ion species, pH and temperature (Aydin et al., 2004; Kirby and Hasselbrink, 2004; Lebron et al., 1993). By adding electrolytes, the ζ-potential diminishes due to more cations in the Stern layer, and the clay flocculates (Chorom and Rengasamy, 1995). However, Dang (2018) demonstrated for three contrasting soils that the EC effect on ζ-potential was well explained by a general equation and had little effect above 2.0 dS/m. When the pH increased from 5 to 9, the ζ-potential of a Silver Hill illite was doubled at SAR>15 (Lebron et al., 1993). The higher the valency of the cations within the Stern layer, the more effective it is in altering the ζ-potential to favour a stable soil environment (Lal and Shukla, 2004). Due to the high specific surface area, and surface reactivity of clay colloidal suspensions, small additions of Na can greatly affect ζ-potential on Ca montmorillonite, resulting in rapid change towards a dispersive soil environment (Bar On et al., 1970; Delgado et al., 2007). On this basis, it is evident that the ζ-potential is a key consideration for any future soil stability investigations.

2.5.1.2. Attractive forces: van der Waals interaction

The attractive forces in DLVO theory originate from van der Waals forces between two clay particles (plates). Table 2–7 provides the van der Waals interaction energy and attractive pressure between surfaces for the mica-water-mica system in relation to distance of separation and plate thickness (Quirk, 1994). As noted, the interaction energy and pressure decreased markedly with increasing distance of separation and that beyond 1 nm separation these quantities were relatively small. The distance of separation was critical in determining the van der Waals interaction energy and attractive pressure. For distance of separation of 1 nm or less, the energy and pressure of interaction were similar for plate thickness (t) =1 nm and t>>D (distance of separation), where 1 nm was the thickness of an elementary aluminosilicate layer (montmorillonite or vermiculite). In addition, the van der Waals forces were also strongly dependent on surface charge density of the clay crystals (Quirk, 2001).

Table 2–7 van der Waals interaction Energy and Attractive Pressure between surfaces for the mica-water-mica system in relation to distance of separation (D) and plate thickness (t)(Quirk, 1994).

	Surface separation (nm)				
	0.25	0.5	1.0	2.0	4.0
Energy (mJ/m^2)					
t=1 nm	-8.7	-1.9	-0.36	-0.05	-0.006
t>>D	-9.3	-2.3	-0.6	-0.15	-0.04
Pressure (MPa)					
t=1 nm	74	8.7	0.9	0.08	0.005
t>>D	75	9.3	1.2	0.15	0.018

2.5.1.3. The application of DLVO theory and its limitation

The traditional DLVO theory, based on the Poisson-Boltzmann (PB) model, can make reasonable predictions for free swelling clay systems, notably Na and Li montmorillonites. DLVO theory prediction is in line with the swelling of Na-montmorillonite, as the basal spacing (d_{001}) values of Na-montmorillonite vary with electrolyte concentration, increasing from 1.9 nm in 0.5 M NaCl to 4.3 nm in 0.3 M NaCl and thereafter increasing further with decreasing concentration (Kjellander et al., 1988). In addition, Quirk and Marcelja (1997) proved that the PB and the DLVO double layer theory satisfactorily described the swelling of Li$^+$ montmorillonite in water and 10^{-4} to 1 M LiCl solutions at swelling pressures of 0.05–0.9 MPa. This was demonstrated with a 0.55 nm thick Stern layer, a Stern potential ranging from -58 mV (0.1 M LiCl) to -224 mV (10^{-4} M LiCl) and a Gouy plane charge of 0.038 Cm^{-2} which is approximately 30% of the layer charge.

However, several authors have argued that the attractive force in clay-colloid interactions is electrostatic, rather than the van der Waals force, as they believed that the attractive van der Waals force could not operate in water over the distances necessary to explain particle-particle attraction (Langmuir, 1938; MacEwan, 1948; McBride, 1997). The Hamaker constant in water (2.2×10^{-20}) determined experimentally for mica surfaces, which is used to calculate the attractive van der Waals pressure, was significantly smaller than that in air 13.5×10^{-20} (Israelachvili, 2011). While a merging of double layers upon particle approach would cause redistribution of couterions into a single layer to minimize free energy, and result in an attractive electrostatic force (Langmuir, 1938; MacEwan, 1948), the DLVO theory is unable to consider the counterions as mobile species. This is partly why DLVO cannot explain the limited swelling phenomenon of Ca-montmorillonite over a very wide range of $CaCl_2$ concentration (Kjellander et al., 1988; Norrish, 1954; Quirk et al., 1986). The Ca-montmorillonite crystals did not swell to the extent as Na-montmorillonite and maintained a high permeability even to distilled water, which is the basis of the potential minima, or potential well, discussed in detail by Quirk (2001). This absence of swelling was confirmed by Norrish and Quirk (1954) using X-ray diffraction measurements which revealed that in $CaCl_2$ solutions with concentration less than 1 molar, and in distilled water, the d_{001} X-ray spacing remained at 1.9 nm. Kjellander et al. (1988) have explained the restricted Ca-smectite swelling by a fluctuating electrostatic force whose time-averaged value is attractive.

DLVO theory has limitations explaining two plates approaching. Consequently, only at large particle separations, where diffuse double-layer overlap is small, can the DLVO model can be expected to produce a good approximation of the potential energy (McBride, 1997). Furthermore, the DLVO model assumes that the ions obey the Boltzmann equation and interact only via a “mean potential”, which predicts that the double layer interactions depend only on the valence of the electrolyte ions, regardless of their nature (Manciu and Ruckenstein, 2003). However, it is well documented that different electrolytes of the same valence have different effects on clay colloidal behaviour. Thus, it is clear that there are deficiencies in the DLVO model that require further investigation as investigations to date have not provided a unified model capable of predicting the full range of phenomena discussed above.

2.5.2. Beyond DLVO theory: specific ion effects

As noted, in dilute electrolytes (low ionic strength) or acid solution, the surface force versus the separation distance of some clay particles follows DLVO theoretical prediction (Hartley et al., 1997; Quirk and Marcelja, 1997). However, DLVO theory has its limitations, which are often problematic for experiments at short ranges (<10 nm) (Boström et al., 2001; Shubin and Kékicheff, 1993). Consequently, DLVO cannot explain why two different salts with the same ionic valence exhibit different effects on colloid dispersive behaviour. This is mainly because DLVO theory does not take into account the specific ion effects. Many researchers have demonstrated that most specific ion effects can be explained theoretically by including ion-ion, ion-colloidal dispersion forces and ion hydration (Karraker and Radke, 2002; Manciu and Ruckenstein, 2003; Pashley and Quirk, 1984).

In very dense electrolytes, an additional strong repulsive force at short distances between mica surfaces in different electrolyte solutions has been observed, termed as the hydration force, which prevents van der Waals attractive collapse between two mica surfaces (Leng, 2012; Pashley, 1981; Pashley and Israelachvili, 1984). The hydration force was observed only above a critical concentration and was different for each cation, *e.g.* $\geq$1.0 M for divalent cations (Pashley and Israelachvili, 1984). Israelachvili and Adams (1978) also reported the existence of an additional repulsive force when two mica surfaces are at small distance (<7.5 nm), without any association to DLVO theory. The magnitude of the additional force is found varying between mica types and is largely independent of electrolyte concentration (Israelachvili and Adams, 1978). Furthermore, the existence of a strong repulsive hydration force at a short distance within colloidal silica (SiO_2) has also been detected by means of surface force apparatus (SFA) and atomic force microscopy (AFM) (Valle-Delgado et al., 2005). The authors claimed that this short-range repulsion could be responsible for the suspension-stability of silica suspensions at high electrolyte concentrations (Valle-Delgado et al., 2005). Israelachvili and McGuiggan (1988) reported that the hydration force, which can be attractive, repulsive or oscillatory, arises from the structuring or ordering of liquid molecules when confined between two surfaces close together. A strong additional attraction at small surface separations has been observed, which is believed to arise from ion-correlation effects when highly charged surfaces interact with divalent counter ions (Israelachvili and McGuiggan, 1988; Kjellander et al., 1988). The ion-correlation forces can be far stronger than the van der Waals attraction, and thus may be crucial in overcoming the double-layer and other repulsive forces between particles and surfaces, thereby promoting their adhesion (Israelachvili and McGuiggan, 1988). Valle-Delgado et al. (2005) emphasized that the origin of the short-range repulsive hydration forces may vary in different systems (mica, lipid bilayers, silica, proteins, etc.). Each system associates with the hydration forces different mechanisms, including polarization of water molecules by surface dipoles, changes in the dielectric constant of the medium, adsorption of counterions, and breakage of hydrogen bonds. This details that moving beyond the DLVO theory is a complex process, likely to be highly soil-specific and solute-specific.

Boström et al. (2001) reported that different cations or anions with the same valence can produce significantly different coagulation effects for colloidal-sized particles, and these effects are referred to as the Hofmeister effect, or specific ion effect. Specific ion effects are closely related to hydration, quantum fluctuations (or ion-colloidal dispersion forces), surface charges (Liu et al., 2014), as well as the specific properties of ions, including their size, electron shell number and ability to be polarized, which directly influence their electron configuration and atomic and molecular orbitals (Parsons et al., 2011). A recent study showed that the fundamental mechanism for the specific ion effect is not hydration effects, but quantum fluctuation forces which cause the London-Lifshitz dispersion forces (Parsons et al., 2011). Even hydration itself is determined by quantum fluctuation forces or dispersion forces (Parsons et al., 2011). Xu et al. (2015) further disproved that specific ion effects are caused by the ionic hydration and dispersion forces. Instead, they have shown that the difference in polarization between the same valence ions (K^+ and Na^+) at the charged clay surface was responsible for the specific ion effects. The authors termed it as non-classical polarization, and this strong non-classical polarization of the adsorbed cation decreased the electric field and the electrostatic repulsion between adjacent particles in the aggregates, and thus strongly increased the aggregate stability.

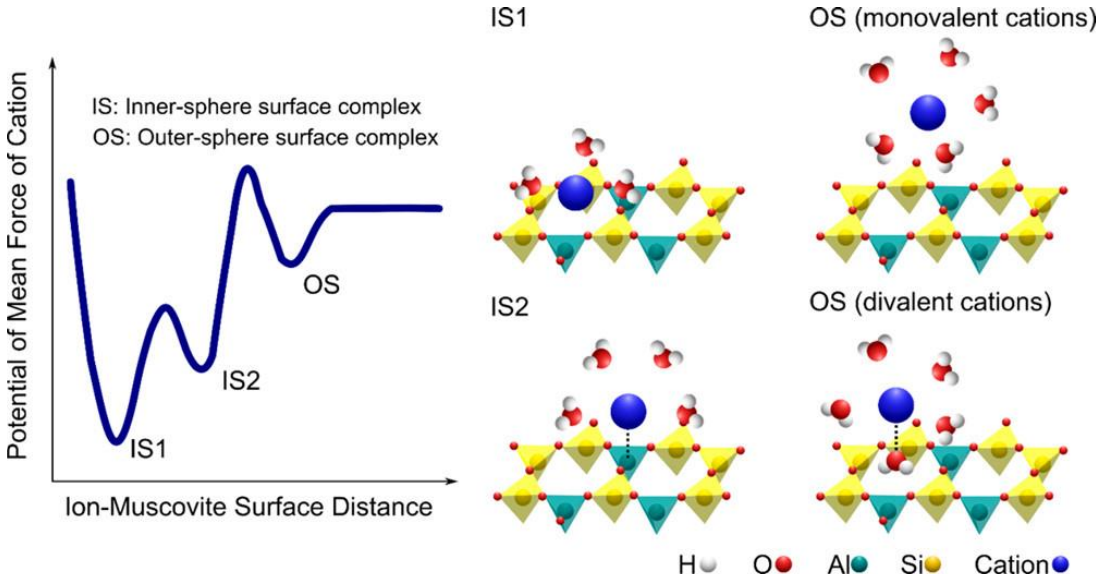

Fig 2–14 The schematic diagram of inner-sphere (IS1, IS2) and outer-sphere (OS) surface complex (Kobayashi et al., 2017)

Kobayashi et al. (2017) believed that the ion-specific interaction must be understood at the molecular, rather than the mean-field level. This is because mean-field theories such as the classical Gouy−Chapman theory and DLVO theory have limitations in describing certain phenomena concerning the Stern layer, *i.e.* charge reversal, adsorbed ion-ion correlations, and hydration forces. The authors simulated the possible presence of eight ions (Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) on the inner-sphere and outer-sphere surface complex of muscovite mica. The inner-sphere surface complex (inner part of Stern layer) is further categorized in a ditrigonal cavity (IS1) and that on top of Al (IS2). The possible presence of hydrated cations is shown in Fig 2–14. These authors found that Na^+, Ca^{2+}, Sr^{2+}, and Ba^{2+} can form both IS1 and IS2; K^+, Rb^+, and Cs^+ can form only IS1; and Mg^{2+} can form only IS2. It is suggested that the formation of IS1 and IS2 is governed by the charge density of the ions. Among the eight ions, the hydration structure for the outer-sphere surface complexes of divalent cations differs from that of the monovalent cations by one adsorbed water molecule (*i.e.* a water molecule located in a ditrigonal cavity) (Kobayashi et al., 2017).

In summary, the mechanisms of specific ion effects remains unclear, as indicated by numerous competing theories and sometimes contradicting results. However, these investigations demonstrate that different ions have specific effects on clay colloidal behaviour, and emphasise that ion valency, size and ability to be polarized are important factors which are worth looking at.

2.5.3. Ionicity concept

Marchuk and Rengasamy (2011) introduced the ionicity concept by consideration of the cation size, valency and its ability to be polarized, and illustrated that the chemical bond between cations and clay particles is a mixture of covalent and ionic bonds (electrostatics). The ionic concept goes beyond DLVO diffuse double layer theory by saying that the degree of covalency in cation binding is also important, not just electrostatics, and in this way it approximates the specific ion effect of Na from K, and Ca from Mg (Smith et al., 2015).

The attractive interaction between one ion and another of opposite charge strong enough to form a chemical bond is termed an ionic bond. In contrast, covalent bonds involve a significant distortion of the electron configurations (orbitals) of the bonding atoms that results in the sharing of electrons. Inevitably, any chemical bond shows some degree of ionic character and some degree of electron sharing (covalent character) (Pauling, 1960) .

Sposito (2008) suggested Mg-O and Ca-O bonds in clay minerals are considered 75% to 80% ionic, whereas Na-O and K-O bonds are 80% to 85% ionic. Similarly, in the colloidal system, clays can be considered as large sized anions with high charge, where both charge and size is several times larger than the cations (Marchuk and Rengasamy, 2011). Thus, it is reasonable to assume that the bonding between the hydrated cation and clay is a mixture of ionic and covalent bonding.

To calculate the degree of ionic and covalent bonding, Marchuk and Rengasamy (2011) combined ionic potential (which scales the valence by cation radius) and Misono softness parameters (the energy required to extract an electron from a cation, a measure of the covalency of cation binding) by multiplication into the covalency index (CI; Eq 2.7), and then subtracted this from 1 to obtain ionicity index (II; Eq 2.8).

$$Covalency\ index\ (CI) = (I_Z/I_{Z+1})Z^{0.5} \qquad \text{(Eq. 2.7)}$$

$$Ionicity\ index\ (II) = 1 - CI \qquad \text{(Eq. 2.8)}$$

From Equation 2.7, where a cation with a valence Z and whose ionisation potential is I_Z, and I_{Z+1} is the ionisation potential when the valence of the cation changes to $Z+1$.

The authors found that the ζ-potential of the homoionic clays decreased following the decrease in the ionicity of the cation, irrespective of different clay minerals (Marchuk and Rengasamy, 2011). As the degree of ionicity decreased, the mean particle size of clays increased supporting the notion that increasing covalency of clay–cation bonds leads to aggregation of clay particles. Furthermore, Marchuk and Rengasamy (2011) experimentally confirmed that the surface charge of clays may influence the ionicity of clay–cation bonds. The ionicity indices indicate the relative theoretical difference between cations. The authors demonstrated that, using two soil clays and two pure clays, the degree of clay cation bonding varies due to different clay minerology and clay surface charge. Further investigation is required into using the ionicity concept in prediction of soil clay dispersion and structural stability for different types of soils.

2.6. Processes involved when a dry aggregate of soil is wetted

This section describes the four stages of structural change that occur when a dry aggregate of soil is wetted, including: 1) dry aggregates, 2) swelling and disaggregation, 3) dispersion, and 4) flocculation of dispersed clay. In dry aggregates, clay particles are bound together by organic and inorganic compounds (stage 1), which produce strong attractive pressures of up to mega Pascals, as shown in Fig. 2–15 (Rengasamy and Sumner, 1998). At this stage the clay surfaces may have at least one layer of adsorbed water molecules and the distance between any two adjacent clay particles is generally less than 1 nm (Rengasamy and Olsson, 1991).

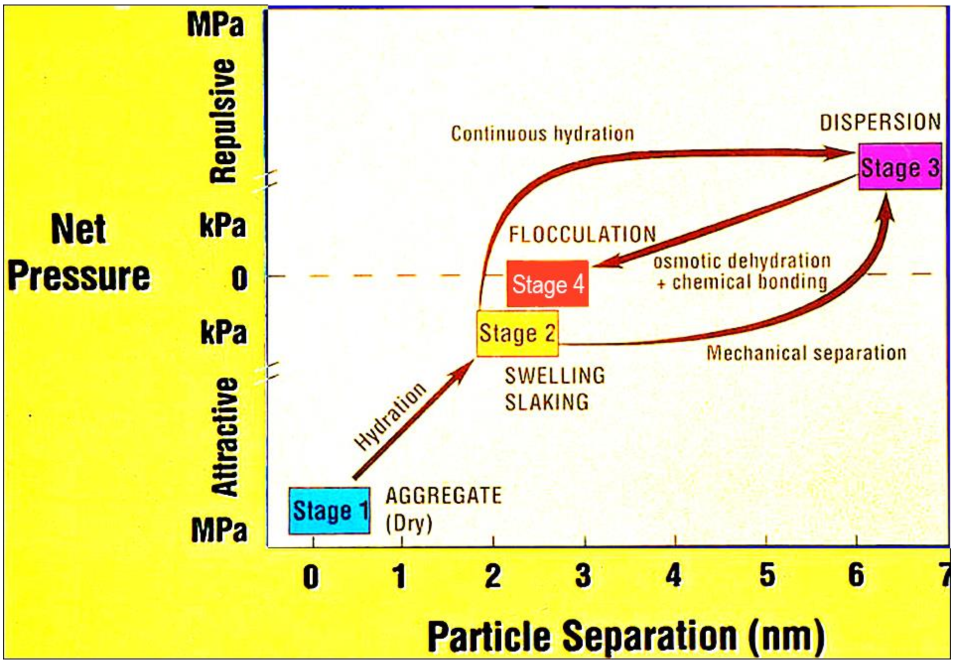

Fig. 2–15 Illustration of the process taking place when a dry aggregate is wetting (Rengasamy and Olsson, 1991; Rengasamy and Sumner, 1998)

Upon wetting, intra-crystalline swelling may occur within the smectite quasicrystal, where the individual clay layers expand in steps corresponding to monolayers of water. Clay layer hydrates with 0, 1, 2, 3, and 4 layers of water molecules are distinguished by d_{001} (basal) spacings of approximately 1, 1.25, 1.5, 1.75 and 2 nm, respectively (Laird, 2006). A limited increase of d_{001} spacing has been observed in Mg and Ca montmorillonite clay, from 1.62 to 1.92 nm for Mg (8 M $MgCl_2$ to H_2O) and 1.54 to 1.89 nm for Ca (8 M $CaCl_2$ to H_2O) (Norrish, 1954). Similarly, an expansion of d_{001} spacing from 1.55 to 1.84 nm occurred in Na saturated smectite, as the NaCl concentration was reduced (Slade et al., 1991).

Intra-crystalline swelling is a process that occurs within quasicrystals. In contrast, double-layer (osmotic) swelling, termed as inter-crystalline swelling, is a process that occurs between quasicrystals. When the ionic strength of the equilibrium solution is decreased, the repulsive pressure increases while the attractive pressure decreases due to the development of diffuse double layers. Consequently, the distance between the clay particles increases. Before clay dispersion occurs, this process with increasing distance between clay particles is termed as disaggregation. In this stage, the attractive forces prevail in-between clay particles, but the repulsive forces are effectively weakening the attraction. Thus, it is important to draw the parallel between the double layer development and the aggregation-disaggregation-dispersion boundary condition. Rengasamy and Sumner (1998) suggested that clay particles beyond 7 nm distance result in clay dispersion (stage 3). Once complete clay dispersion takes place, electrostatic repulsive forces are operative and attractive forces become insignificant.

The double-layer (osmotic) swelling is influenced by the nature of exchangeable cations, solution concentration, clay charge density and origin. Norrish (1954) reported the interlayer spacing of Na montmorillonite in 0.3 M NaCl had two values as 1.9 nm (crystalline swelling) and4 nm, and in more dilute solutions d_{001} increased linearly with respect to $C^{-1/2}$, where C is solution concentration. The expansion from 2 nm to >3 nm is associated with the formation of diffuse double layers and the consequent change of the electrostatic attractive force to a (osmotic) repulsive one. The work from Posner and Quirk (1964) and Slade and Quirk (1991) showed that for Ca and Mg saturated smectites, the change in basal spacing from 1 to 1.55 nm is not affected by the electrolyte concentration, while the ionic strength below (basal spacing from 1.5 to 1.9 nm) can be regarded as an osmotic effect, depending on the charge density and origin (tetrahedral or octahedral) in smectites. However, Laird (2006) suggested that the surface charge density of smectites has almost no effect on the electrostatic repulsive force between quasicrystals and hence on the stability of smectite suspensions. Most quasicrystals of low-charge Na smectites will spontaneously break up so that diffuse double layers form and separate the individual smectite layers when placed in a low ionic strength solution. For high-charge Na-smectite, some quasicrystals will remain intact, but most will at least partially break up. Laird (2006) further suggested both ionic strength and valence have much greater influences on the relationship between the local electrical potential and distance than clay surface charge density and origin. These results suggest that ionic type and valence could play a critical role in deciding the clay colloidal behaviour, as proposed in the ionicity concept.

Clay quasicrystals can behave differently when subject to mechanical stress. As noted, the Mg and Ca quasicrystals do not spontaneously delaminate. Only mechanical stresses may cause some big quasicrystals to break up, forming a suspension of smaller Ca- or Mg-smectite quasicrystals (Laird, 2006). In contrast, for a Na/Ca-smectite system, demixing can happen (Laird and Shang, 1997). Na ions tend to be segregated in certain interlayers while the competing Ca ions are segregated into other interlayers (Laird, 2006). When the clay is shaken, the quasicrystals readily break apart at interlayers dominated by Na (Fig. 2–7), leading to the formation of two types of particles: (1) ≈1.0 nm thick, Na^+-based individual 2:1 layers as single particles, and (2) particles with Ca^{2+} as the dominant interlayer cations. The latter are stacks of parallel 2:1 layers (Kleijn and Oster, 1982; Quirk and Aylmore, 1971), which are relatively stable under shaking, stirring, sonication, and even certain pressure (Tan et al., 2017). The phenomenon of demixing is a major reason why a relatively small amount of Na can be so disruptive to soil structure (Shainberg and Otoh, 1968).

Stage 4 represents the point of net zero pressure whereby the attractive and repulsive forces are balanced. Two quasicrystals with sufficient kinetic energy to overcome the double layer repulsion (and other repulsive forces), will begin to approach each other in an aqueous suspension. Once the two surfaces become close enough (<4 nm) and enough anions, excess cations and water are expelled from the region between the two approaching surfaces, the electrostatic forces will undergo a complete reversal from being repulsive in the double layer region to attractive in the crystalline swelling region (Laird, 2006). The result is that two quasicrystals join together forming one larger quasicrystal. The attractive pressure necessary to bring the clay particles closer to each other can be provided by the electrolyte concentration in soil solution. A critical flocculation concentration is necessary for the clay particles to flocculate. In addition, altering the pH to the value of point of zero charge will lead clay particles flocculation (Rengasamy and Olsson, 1991). However, it must be noted that this process does not reverse the dispersion process back into an aggregated state, rather a flocculated one. That is, from a practical point of view, it will be important to provide models that can predict the repulsive pressures and their mechanisms, and define the aggregation-dispersion boundary condition. There is also value in understanding the dispersion flocculation processes.

2.7. Conclusion

Magnesic soils, described as soils with elevated magnesium concentration in soil solution and/or cation exchange complex, have been reported world-wide. However, insufficient research has been conducted on magnesic soils, in terms of their definition, distribution and the role of Mg on soil structural stability. Historically, Mg has been considered equivalent to Ca in terms of its effect on soil structural stability. Literature to date has reported that in some soils Mg can result in, or enhance soil clay dispersion (Dontsova and Norton, 2002; Zhang and Norton, 2002), although the actual extent of effect Mg has on soil dispersive behaviour is likely to have been exaggerated (Bennett et al., 2016a). The effect of Mg has been theoretically calculated using flocculation power (Rengasamy and Sumner, 1998), and been applied in the new indices CROSS and EDP in assessing the quality of irrigation water and concomitant soil structural stability (Bennett et al., 2016a; Rengasamy and Marchuk, 2011). However, the flocculation power used in these indices requires further validation before general use (Rengasamy and Sumner, 1998). Clay behaviour in suspension is related to the degree of ionicity of clay-cation bonds, including Mg clays. The proportion of ionic bonding (electrostatic attraction) and covalent bonding involved in cation–clay interaction determines clay dispersive behaviour. To provide a sound answer to the effect of Mg on soil structural stability, factors such as cationic composition on the exchange sites, soil pH, EC, as well as clay content, mineralogy and organic matters, need to be taken into consideration. The clay surface net charge changes as pH varies, while the degree of variation may be different due to different clay minerals and organic matter. To that end, determining the specific effect of Mg on soil structural stability is rather complex and will require a number of key considerations.

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3. Rapid method for assessment of soil structural stability by turbidimeter

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3.1. Abstract

A rapid and inexpensive method to evaluate soil structural stability via assessment of soil clay dispersion is needed. Such a method would provide critical information for decision making for soil and agricultural management not currently undertaken, due to the expense of testing. The aim of this work was to validate the use of a turbidimeter for quantifying clay released from soil and to relate this back to dispersive parameters. Ten Australian soils with different physico-chemical properties were studied. Six-step dilution was used to adjust the clay suspensions sequentially by dilution from a datum concentration of 4000 NTU. The linearity of turbidity by dilution was verified, considering the effects of soil colour and mean particle size. There was a strong correlation between turbidity (NTU) and dispersed clay (mg L^{-1}, % of soil) for each soil. Clay particle size was related to turbidity response, although the coefficients between turbidity and dispersed clay were very close irrespective of mean particle size differences. Dispersed clay was concluded to be accurately quantified using a turbidimeter after spontaneous and mechanical dispersion. A semi-quantitative dispersion assessment chart was developed for rapid assessment of soil structural stability, the application of this which is intended to provide rapid diagnosis and act as an important index for soil management practitioners. Additionally, when dispersed clay was combined with electrical conductivity (EC) and clay content parameters, the dispersive indices (cation ratio of soil structural stability and exchangeable dispersive percentage) were reasonably predicted at a resolution useful for farm management decisions.

3.2. Introduction

Soil clay dispersion can largely affect soil structural stability. In most cases, soil clay dispersion reduces pore volume and continuity, which leads to surface crusting, low soil infiltration, poor seedlings emergence and decreased crop productivity (Oster and Shainberg, 2001; So and Aylmore, 1993). The formation of a surface crust is the result of two integral mechanisms: (1)

physical disintegration of soil aggregates, which is mechanical in nature and caused by kinetic energy (e.g. raindrop impact and tillage operations); (2) physico-chemical dispersion of the clay particles (Agassi et al., 1981; Levy, 2012; Morin et al., 1981; Sumner, 1993). The factors affecting clay dispersion have been documented as soil cation composition, electrolyte concentration, clay content and mineralogy, organic matter, soil pH and mechanical stress (Chi et al., 1977; Chorom et al., 1994; de Menezes et al., 2014; Ezlit et al., 2013; Frenkel et al., 1978; Goldberg et al., 1988; Nelson et al., 1999; Rengasamy, 1983; Rengasamy and Marchuk, 2011). Spontaneous and mechanical dispersion is a set of measurements of clay dispersion which consider the physico-chemical properties of soil and the impact of kinetic energy, respectively, and can provide quantitative measurement of dispersed clay (Rengasamy, 2002; Rengasamy et al., 1984).

Determining an amendment strategy for sodic soil relies on a measure of soil sodicity (or dispersibility) – usually the sodium adsorption ratio (SAR) in America, or the exchangeable sodium percentage (ESP) measurement in Australia in conjunction with the electrolyte concentration, to govern the type and amount of amendment required; i.e, gypsum, calcium chloride and/or calcium carbonate (Bennett et al., 2014a; Bennett et al., 2014b; Qadir et al., 2001). However, soil sodicity measurement, as soil solution or exchange, is time-consuming and costly (Rengasamy and Churchman, 1999). Additionally, there are large differences between measurements of exchangeable cations made on the same samples in different Australian laboratories, which is often due to the analysis method and the varying soil physical-chemical properties (Rengasamy and Churchman, 1999). More recent studies have shown that potassium (K^+) and magnesium (Mg^{2+}) ions in solution or on the exchange complex can also affect clay dispersion even when the sodium (Na^+) levels are very low (Bennett et al., 2016a; Rengasamy and Marchuk, 2011). Therefore, using SAR or ESP as the indicator of soil amendment can be misleading. From this point of view, using dispersed clay as an indicator is in fact more meaningful and straightforward. Rengasamy et al. (1984) proposed a threshold of 1% mechanically dispersed clay, or less, as desirable for minimum aggregate breakdown in the field; soils with dispersed clay above this level likely require amendment.

Dispersed clay can be directly measured gravimetrically or proximally via spectrophotometry, such as turbidimetry (Kay and Dexter, 1992; Marchuk et al., 2013a; Rengasamy et al., 1984). Compared to the gravimetric approach, turbidimetry is more efficient and requires only a small volume of clay suspension, enabling detection at 90^o to the suspended particulate in water by light scattering, which is a recognized EPA Method 180.1 (O’Dell, 1993). As a potential alternative method to the gravimetric approach, however, turbidimetry cannot directly quantify clay concentration in a colloidal system. The relationship between turbidity and dispersed clay content has been studied, with significant correlations detected (Amézketa and Aragüés, 1995a; Dexter and Czyz, 2000; Holliday et al., 2003). However, linear coefficients of prediction varied in the different reports. One reason may be related to the different light sources used in turbidimeter (Hongve and Åkesson, 1998). Alternatively, the inconsistent coefficients may be related to the method of measuring the real clay content. Czyz et al. (2002) used the conventional hydrometer method to measure dispersed clay, which is further correlated to the measured turbidity. Holliday et al. (2003) used the fractional clay obtained after oven-drying – rehydrating process, and claimed that the relationship between turbidity and dispersed clay may not be linear. Clay suspension from different soils with differing texture, size, shape, colour and reflectivity of the particles may determine the spatial distribution of the scattered light intensity, and hence likely have an influence on the relationship between turbidity and clay content (Bin Omar and Bin MatJafri, 2009). The unclear relationship between the turbidity and clay content deserves further attention, and the weight of the affecting factors, as mentioned above, should be re-considered to understand the reliability of this testing method.

The aim of this investigation was to develop a relationship between turbidity measurement and the quantity of dispersed clay for soils in general. Physical and chemical factors affecting this relationship were subsequently investigated, with the intention of producing a rapid assessment index of dispersed clay for practitioners.

3.3. Materials and Methods

3.3.1. Soil used

Ten soil samples collected from Queensland and South Australia, as shown in Table 3–1, were used in this study. The physical and chemical properties of soil samples were determined using standard procedures: soil pH (4A1), electrical conductivity (EC) (3A1), exchangeable cations and effective cation exchange capacity (CEC_{eff}) (15A2) were determined as per Rayment and Lyons (2011); the sodium adsorption ratio (SAR) and cation ratio of soil structural stability (CROSS) were calculated (Rengasamy and Marchuk, 2011); the exchangeable sodium percentage (ESP) and the exchangeable dispersive percentage (EDP), which incorporates the dispersive effects of sodium (Na), potassium (K with dispersive effect as 0.556 of Na) and magnesium (Mg with dispersive effect as 0.037 of Na) comparing to ESP, were calculated

(Bennett et al., 2016a); particle size distribution was determined using the method of Gee and Bauder (1986); whilst water dispersible clay content was measured in accordance with FAO (2014); and clay mineralogy was determined by X-ray diffraction. A Munsell soil colour chart was used to determine soil colour of dry aggregates. The characterisation results of the soils using these methods are presented in Table 3–1.

Table 3–1 Physical and chemical properties, main clay minerals, classification, texture, colour and soil locations of the studied soils

Soil	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Depth (cm)	0-10	20-30	10-20	15-40	15-40	0-10	0-10	0-10	0-10	0-10
pH	6	5.7	6.3	7.4	6.8	8.6	6.8	7.5	7.5	6.9
EC (dS m^{-1})	0.07	0.21	0.15	0.05	0.15	0.14	0.36	0.17	0.09	0.23
CEC$_{eff}$ (cmol$_c$ kg^{-1})	4.22	12.6	9.3	14.4	15.8	43.4	42.4	42.3	36.6	20.6
SAR	1.8	4.0	2.2	0.3	0.4	1.2	0.3	1.6	1.3	0.9
CROSS	2.1	4.5	2.4	0.5	0.9	1.4	0.4	1.8	1.5	1.0
ESP (%)	8	9.8	6	0.6	0.7	2.1	0.4	2.3	2.8	1.2
EDP (%)	11.1	12.2	8.6	5.8	7.8	4.5	3.3	5.0	5.7	4.1
Organic carbon (%)	1.0	1.3	1.2	0.7	2.9	1.1	1.3	1.0	1.0	1.0
Dominant clay mineral†	K	K, M	K, M	I, K	M	M	M	M	M	M, K
Taxonomic class‡	Red Oxisol	Grey Alfisol	Grey Alfisol	Red Alfisol	Black Vertisol	Black Vertisol	Black Vertisol	Black Vertisol	Black Vertisol	Black Vertisol
Texture§	Clay	Clay	Clay	Sandy clay	Sandy clay loam	Heavy clay	Heavy clay	Heavy clay	Clay	Sandy clay
Clay content (%)	50	46	38	35	34	68	63	60	58	39
Water-dispersible clay (%)	15	40	30	23	13	33	25	35	35	20
Location	Toowoomba, QLD	Bundaberg, QLD	Bundaberg, QLD	Adelaide, SA	Adelaide, SA	Dalby, QLD	Dalby, QLD	Dalby, QLD	Dalby, QLD	Dalby, QLD
Munsell soil colour (dry)	5YR3/3	10YR6/3	10YR5/3	5YR4/6	10YR3/2	10YR2/1	10YR3/1	10YR3/1	10YR4/1	10YR4/2

† I, illite; K, kaolin; M, montmorillonite
‡ soil classification used the USDA soil taxonomy (Soil Survey Staff, 1999)
§ the texture is determined according to the defining system (FAO, 2014)

3.3.2. Preparation of clay suspension

Forty grams of each soil was placed into a 250 mL bottle, mixed with 200 mL of deionised water, and shaken for 12 hrs on an end-over-end shaker. The suspension was transferred into a 1 L measuring cylinder and topped up to 1 L with deionised water. The top 800 mL of clay colloidal suspension was collected after 24 hrs (Lal and Shukla, 2004). A 53 µm sieve was used to remove visible organic matters from the colloidal suspension. By adding deionized water, turbidity of soil clay suspensions were adjusted to a datum concentration of 4000 NTU, which corresponds to the upper limit of the Hach Turbidimeter 2100N. A six-step dilution procedure was used by sub-sampling the 4000 NTU datum clay suspension to 75%, 50%, 25%, 12.5%, 6.25% and 2.5% by addition of deionised water.

3.3.3. Dispersed clay quantification

Clay content was quantitatively determined for the datum and the subsamples to measure true dilution percentages. An amount of 400 mL soil clay suspension was taken from the datum or the subsamples, and transferred into pre-weighed containers accordingly. The samples were dried in an oven at 105^{o}C for 48 hrs. The weight of dried clay was obtained volumetrically by accounting for the initial volume of the subsample. All weighing was performed using a four-digit scale in two replicates.

3.3.4. Particle size analysis

The mean particle size of the clay suspension was determined by dynamic light scattering spectroscopy using a Malvern Zetasizer Nano-ZS analyser at 25^{o}C. This diameter is an intensity-weighted average particle size (z-average), which was calculated as the mean of 3 measurements and each measurement was averaged over 13 individual measurements performed automatically by the instrument. The soil clay suspensions of 2000 NTU and 100 NTU turbidity were selected for mean particle size analysis for the ten soils.

3.3.5. Turbidity measurement

3.3.5.1. Theoretical background

The turbidity, τ, of a monosized suspension of nonabsorbing isotropic sphere particles, is defined by

$$\tau = \frac{N\pi D^2}{4} Q(\frac{\pi D}{\lambda_m}, \frac{n_p}{n_m}) \qquad \text{[Eq.3.1],}$$

where τ is a function of the particle number per volume, N, the dimensionless particle size, D, and the scattering coefficient Q. This scattering coefficient is defined as the ratio of the scattering to geometrical cross sections, which is a function of the particle size D, the wavelength of the incident wave in the medium λ_m, and the ratio of the refractive index of the particles n_p to the refractive index of the medium n_m (Kissa, 1999; Melik and Fogler, 1983).

Equation [3.2] is applicable for turbidity calculation of a suspension of nonabsorbing sphere particles with various particle sizes

$$\tau = N \int_0^{\infty} \frac{\pi D^2}{4} f(D) Q(\frac{\pi D}{\lambda_m}, \frac{n_p}{n_m}) dD \qquad \text{[Eq. 3.2],}$$

where *f(D)* is the normalized particle size distribution function, i.e., *f(D)dD* is the number fraction of particles with a size between *D* and *D+dD* (Kissa, 1999; Melik and Fogler, 1983).

For a given suspension and turbidimeter, the particle size (*D*), refractive index of the particle (n_p), the refractive index of the medium (n_m) and the wavelength of incident light in the medium (λ_m) are constants. If the size distribution of the particles *f(D)* and particle size *D* are assumed to be unchanged during dilution, the turbidity of a suspension is a function of particle number (*N*) per unit volume, which is proportional in dilution. Therefore, the turbidity of a given suspension is theoretically linear to the concentration.

3.3.5.2. Measurement

Turbidity measurements were performed on a Hach Turbidimeter 2100N, which is designed to meet the reporting requirements of EPA Method 180.1 (D1889-00, 2000; Eaton and Franson, 2005). The turbidity unit is reported in Nephelometric Turbidity Units (NTU). The Hach Turbidimeter 2100N has a capacity to test samples up to 4000 NTU. The diluted clay suspensions were agitated to ensure uniform mixing and immediately placed into a turbidimeter cell. Gelex® Secondary Turbidity Standards were used for instrument calibration prior to measurement to ensure calibration.

3.3.6. Assessment of clay dispersion

The assessment of clay dispersion includes two methods: spontaneous and mechanical dispersion, which were modified from the methods described by (Marchuk et al., 2013a; Rengasamy, 2002). Five grams of air dry soil (<2 mm) were placed into a turbidimeter cell, with 25 mL of distilled water being added slowly to avoid disturbance of the soil. The cell was carefully and slowly inverted three times to simulate spontaneous dispersion, or twenty times to simulate mechanical dispersion. After sitting for 4 h, the turbidity was measured with light passing through a 5 cm depth of soil clay suspension. When the turbidity was beyond the capacity of the turbidimeter (>4000 NTU for the machine used in this study), 5 mL of clay suspension at depth of 5 cm were carefully pipetted out and diluted in another turbidity cell. The turbidity of the diluted sample was then measured and recorded together with the dilution factor.

3.4. Results and discussion

3.4.1. The effect of dilution on turbidity measurement

The turbidity testing results of six-step dilution from the datum clay suspension (4000 NTU) are plotted as one sample population, where the $y=x$ line, the min, mean and max data of each-step dilution are demonstrated in Fig. 3–1. The measured turbidity at each dilution is very close to the targeted turbidity.

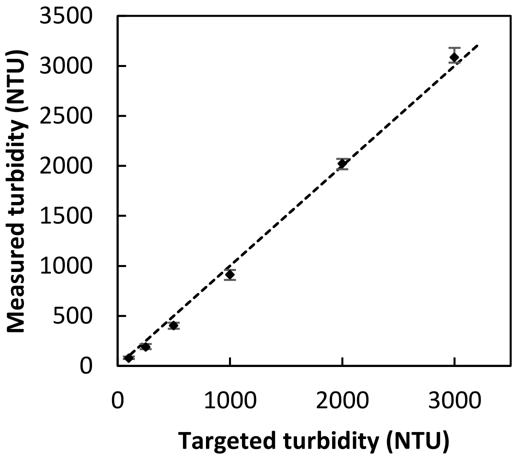


Fig. 3–1 All measured turbidity of six-step dilution as one sample population, where the y=x line is demonstrated, the mean data is indicated as ♦, the max and min data are indicated by the scale bar.

The regression results between the measured turbidity (y) of the clay colloidal suspension and the expected turbidity (x) by each soil are given in Table 3–2. The slope (a) of the linear trend lines of ten soils ranged between 0.997 and 1.034. The highly linear relationship is further demonstrated by the high correlation coefficients R^2 with average value of 0.995.

Table 3–2 The relationships between measured turbidity (y) and targeted turbidity (x) of each clay suspension at six-step dilution are in the form y = ax, where a is the fitting coefficient

Soil	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**Red**	**Grey**	**Black**	**Ave**
a	1.004	1.004	1.034	1.029	1.000	0.998	0.997	1.028	1.014	0.997	1.021	1.019	1.006	1.011
R^2	0.998	0.993	0.996	0.997	0.998	0.993	0.997	0.995	0.994	0.992	0.999	0.996	0.997	0.995

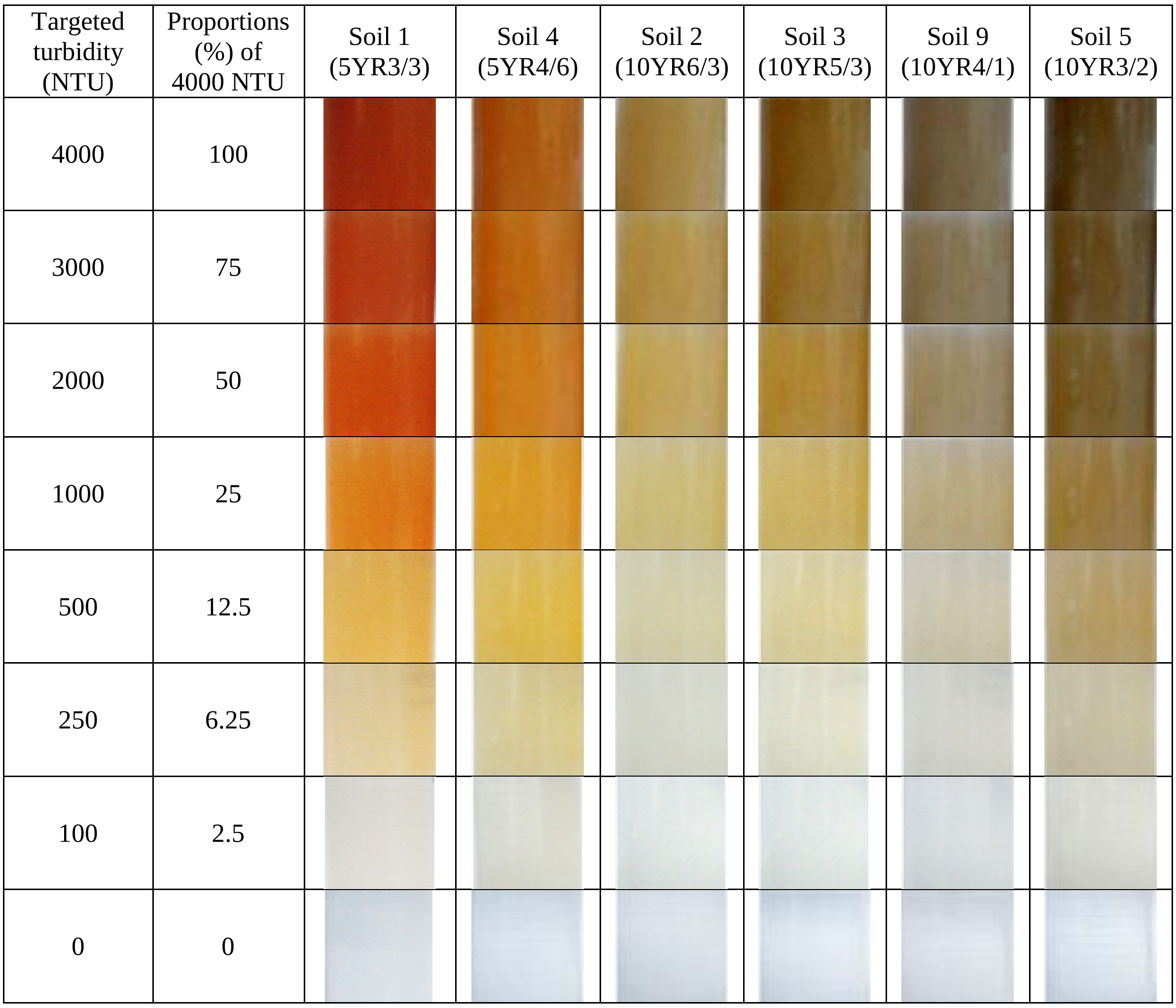
In the *Theoretical background*, the linear relationship between turbidity and concentration is based on the assumption that particle size distribution and particle size are ‘unchanged’ during dilution. The real impact of dilution on particle size was examined for the ten soil suspensions.

As shown in Table 3–3, in the 50% datum solution (with targeted turbidity of 2000 NTU) the mean particle size varies in a range of 303–638 nm while it varies in 261–591 nm in the 2.5% datum solution (with targeted turbidity of 100 NTU). The high correlation (R^2=0.92) of the two sets of mean particle sizes indicates that dilution does not change the particle size (probably size distribution as well). This further justifies the assumption of a theoretically linear relationship between turbidity and concentration from Eq. [3.2]. Moreover, particle size itself seems to have little effect on the linearity of turbidity when comparing the ten studied soils.

Table 3–3 The mean particle size (nm) of ten soils

Soil	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Mean particle size (nm) at 2000 NTU	638	395	377	303	329	465	524	543	458	470
Mean particle size (nm) at 100 NTU	591	373	378	261	291	488	447	429	450	402

Soils vary substantially in colour, hence the potential effect of colour on the linearity of turbidity was also examined. Fig. 2 presents selected colloidal suspensions with contrasting colours (Munsell), in the order of increasing turbidity from top to bottom. Soils 1 and 4 are classified as red, soils 2 and 3 are grey and the remaining soils are black. The regression of measured turbidity (*y*) and targeted turbidity (*x*) of soils with different colours is presented in Table 3–2. The measured response is linear and the R^2 values for the trend lines are 0.999, 0.996 and 0.997 for the red, grey and black soils respectively. Although the slopes of the fitted trend lines decrease from red to black, the absolute values are very consistent, with only ≈2% difference. It is also acknowledged that dark colours absorb more light-waves, while bright colours reflect light-waves, which is coincident with the minor effect of colour on turbidity measurement using a single light detector (Bin Omar and Bin MatJafri, 2009).



Targeted turbidity (NTU)	Proportions (%) of 4000 NTU	Soil 1 (5YR3/3)	Soil 4 (5YR4/6)	Soil 2 (10YR6/3)	Soil 3 (10YR5/3)	Soil 9 (10YR4/1)	Soil 5 (10YR3/2)
4000	100						
3000	75						
2000	50						
1000	25						
500	12.5						
250	6.25						
100	2.5						
0	0						

Fig. 3–2 A full scale of clay colloidal solutions of selected soils in order of increasing turbidity (from left to right) and Munsell soil colour (dry).

Based on the theoretical derivation of Eq. [3.1] & [3.2] and experimental data, it can be concluded that the dilution process is applicable for predicting the turbidity of a high concentrated clay suspension beyond the capacity of a particular turbidimeter.

3.4.2. The relationship between turbidity and dispersed clay concentration

In this study, the relationship between turbidity and dispersed clay concentration was examined and the results are shown in Table 3–4. The R^2 for the linear fits are very high (>0.998), which is in agreement with theoretical analysis as discussed below.

Table 3–4 Relationship between turbidity (τ, NTU) and dispersed clay amount (c, g L^{-1})

Soil	Fitting equation	R^2
1	c=0.393τ	0.9986
2	c=0.689τ	0.9993
3	c=0.765τ	0.9997
4	c=0.749τ	0.9993
5	c=0.739τ	0.9996
6	c=0.644τ	0.9994
7	c=0.599τ	0.9995
8	c=0.680τ	0.9996
9	c=0.648τ	0.9995
10	c=0.585τ	0.9999
Mean	*c=0.649τ*	*0.9754*

The particle concentration *c*, mass per volume, of monosized spherical particles is given by

$$c = \frac{\pi}{6} D^3 \rho N \qquad \text{[Eq. 3.3]},$$

where ρ is the density of particles (Kissa, 1999; Melik and Fogler, 1983).

The particle concentration of spherical particles with various particle sizes can be described by

$$c = \rho N \int_0^\infty \frac{\pi D^3}{6} f(D) dD \qquad \text{[Eq. 3.4]}.$$

By division of Eq. [3.1] and Eq. [3.3], the relationship between turbidity and clay concentration of a monosized spherical particle suspension can be defined as:

$$\frac{c}{\tau} = \frac{2\rho D}{3Q\left(\frac{\pi D}{\lambda_m}, \frac{n_p}{n_m}\right)} \qquad \text{[Eq. 3.5]}.$$

Similarly, by division of Eq. [3.2] and Eq. [3.4], the relationship between turbidity and clay concentration of a polysized spherical particle suspension is given in

$$\frac{c}{\tau} = \frac{2\rho \int_0^\infty D^3 f(D) dD}{3\int_0^\infty D^2 f(D) Q\left(\frac{\pi D}{\lambda_m}, \frac{n_p}{n_m}\right) dD} \qquad \text{[Eq. 3.6]}.$$

Equation [3.5] and [3.6] can be calculated where the particle density (ρ), the particle size *D* and its distribution *f(D),* the refractive index of the particle (n_p) and the refractive index of the medium (n_m), and the wavelength of incident light in medium (λ_m) are known. For a given colloidal suspension, the parameters of ρ, n_p, n_m and λ_m are constants. Because the particle size *D* and its distribution *f(D)* are unchanged during dilution, c/τ is in fact a constant. Hence, for a given colloidal suspension, the turbidity of colloidal suspension is theoretically proportional to concentration (clay concentration). This coefficient c/τ is independent of particle number per unit volume.

The linearity between turbidity and dispersed clay concentration validates the suitability of using a turbidimeter to measure soil dispersion. The dispersion coefficients of the clay suspensions are in a range of 0.393 and 0.765. Compared to other soils, the dispersed clay of Soil 1 is particularly low at equivalent turbidity levels, meaning that less clay particulate in solution is required to contribute the same turbidity effect for Soil 1. The other nine coefficients c/τ of clay colloidal solutions are very close, in the range 0.585 to 0.765.

3.4.3. The effect of particle size on the coefficient c/τ

As described in Eq. [3.5], the particle size is an important parameter affecting the coefficient c/τ. On one hand, the particle size is directly proportional to c/τ. On the other hand, particle size is a major factor affecting the scattering coefficient Q, which is inversely proportional to c/τ. The scattering coefficient Q depends on the particle size parameter ($\pi D/\lambda_m$) in an oscillatory mode, exhibiting a series of maxima and minima. In addition, Q is also dependent on n_p/n_m (Kourti et al., 1991). Hence, the particle size may have a positive or negative effect on c/τ. The line in Fig. 3–3 shows the effect of particle size on the coefficient c/τ at a constant n_p/n_m of 1.2, λ_m of 350 nm and ρ of 2.6 g cm^{-3}. With small sized particles (<300 nm), the size has a very sharp effect, i.e. c/τ decrease significantly with increase in size. At medium particle size (300–1500 nm), c/τ is relatively stable, while large sized particles (1500–2000 nm), as size increases, the c/τ increase sharply again.

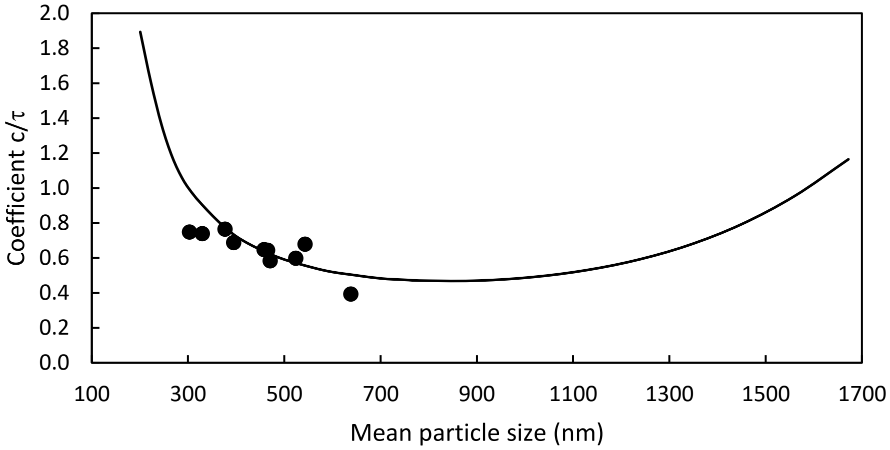


Fig. 3–3 The relationship between particle size and the coefficient c/τ, theoretical relationship as indicated by solid line, experimental relationship plotted by black dots.

The results for the ten soil samples are plotted (solid dots) in Fig. 3–3. The mean particle size of colloidal suspension is slightly inversely proportional to c/τ. This is because the increase of particle size has a higher influence on the scattering coefficient Q than particle size D itself. For example, from the smallest mean particle size 303 nm to the largest particle size 638 nm as shown in Table 3–3, the particle size D increases 2 times, while the scattering coefficient Q increases from 0.55 to 2.15 (≈ 4 times) at λ_m=350 nm and n_p/n_m =1.2 (Pangonis, 1957). Overall, the coefficient c/τ is decreased.

The variation of mean particles size between soils is related to their physical and chemical properties. As noted, Soil 1, sourced from Toowoomba, has extraordinarily large mean particle size. Soil 1 is a basaltic soil formed after volcanic activity (Isbell, 1997; 2016), containing mainly kaolin and iron oxides. The high mean particle size of Soil 1 is likely a result of strong interaction between kaolinite and the (hydro-)oxides of Al and Fe, as the oxides are the putative dominant aggregate stabilizing agents (Oades and Waters, 1991). In comparison, soils 6, 7, 8, 9 and 10 have medium particle sizes, as well as low exchangeable dispersive percentage (EDP <6). As the ESP increases, the aggregation of clay particles will be reduced (Emerson and Chi, 1977). Furthermore, mean particle size of clays increases in the order of Na<K<Mg<Ca, which is related to the ionicity index of clay-cation bonds (Marchuk and Rengasamy, 2011). Therefore, soils with low EDP could be expected to have larger particle sizes than soils with high EDP values (EDP>6). Soil 4 had an EDP value at 5.8 but a relatively low mean particle size at 303 nm compared to Soils 6–10, which can be attributed to its low organic carbon and low electrical conductivity. Organic matter can be absorbed onto the surface of clays and is held firmly by various bonds (Tisdall and Oades, 1982). Therefore, soil containing low organic matter may have low particle size.

Comparing the absolute experimental values of the determined c/τ in this study, it is found that they are relatively constant in the tested size range, which means the real effect of particle size on c/τ is smaller than the theoretical effect. This is because of the particle size distribution (rather than a monosized system), the shape of particles and other factors, such as the organic material, which all have certain effects on c/τ. Therefore, in the medium size region, which covers most cases of real soil clay suspensions, it is reasonable to assume that particle size has little effect on the coefficient c/τ. The average value of the nine tested soils (except for soil 1) is 0.677 (R^2=0.9919, P<0.001), which is very close to the reported value of 0.66 by other researchers (Amézketa and Aragüés, 1995a).

3.4.4. Development of a clay dispersion assessment chart and its application

The strong linearity between the corresponding turbidity value and the determined dispersed clay suggests the suitability of quantitatively measuring dispersed clay concentration by use of turbidimetry. This will be an effective and efficient method for rapid diagnosis of soil structure stability. For this purpose, a user-friendly clay dispersion assessment chart is developed, as shown in Fig. 3–4. The clay percentage is calculated from:

$$\text{Clay }(\%) = 0.677 \times \tau \times \frac{V}{m} \times d \times 100\% \qquad \text{[Eq. 3.7]},$$

in which, 0.677 is the average c/τ obtained from the nine tested soils in this study; m(mg) and V(L) are the soil mass and water volume (combined as a ratio) of the initial soil-water mixture; d is the dilution rate of the mixture for turbidity measurement. It should be noted that if the initial mixture has a turbidity sitting in the measurement range, no further dilution is required, i.e. d=1; if the initial mixture is too concentrated for the turbidimeter, dilution will be necessary.

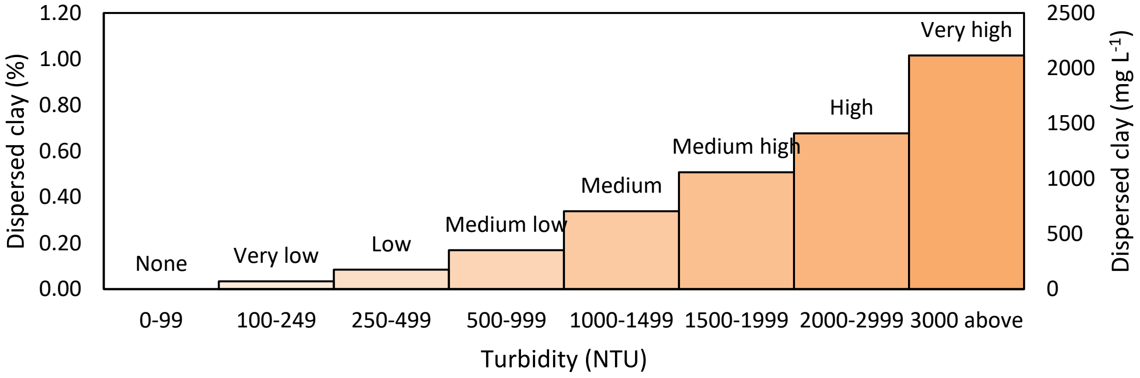


Fig. 3–4 Dispersion assessment chart.

In the dispersion level range from *none* to *low*, soil is relatively stable and amendment can be avoided because extremely low (<0.17%) clay dispersion has limited effect on relative hydraulic conductivity and surface sealing (Yousaf et al., 1987a). In the level of *medium low* to *high*, soil amendment should be considered because an amount of 0.17–1.02% dispersed clay is sufficient to cause substantial reduction in the hydraulic conductivity (Amézketa and Aragüés, 1995b; Yousaf et al., 1987a). Such a small amount of dispersed clay can lodge in the interstitial pores and essentially plug macro-pore pathways within the soil matrix, which leads to the formation of crusts and surface seals (Yousaf et al., 1987a). If dispersion level is in a range of *very high* (>1.02%), amendment is recommended because in this situation, the relative hydraulic conductivity is usually very low; for example, lower than 0.4 (Yousaf et al., 1987a).

To apply the dispersion assessment chart in practise, one should consider the real condition of soil and choose the applicable dispersion method, spontaneous or mechanical. For example, for soil daily maintenance, spontaneous dispersion method can be used to diagnose the stability. If tillage is going to be applied to soil, mechanical dispersion can be used to assess the soil and seek amendment if needed. Table 3–5 lists the turbidity and calculated dispersed clay contents of the ten soils as per the two methods. Different recommendations are made according to different actions to be applied to the soils. ‘Yes’ means amendment is required for the action, ‘Potential’ means amendment should be considered, while ‘No’ means no amendment is required. Applying the dispersion assessment chart indeed provides a rapid diagnosis to receive critical information about the soil stability, which is valuable for soil management.

Table 3–5 Turbidity measured from spontaneous and mechanical dispersion, the dispersed clay and dispersion level and amendment recommendation

Soil ID	Spontaneous dispersion				Mechanical dispersion			
	Turbidity (NTU)	**Dispersed clay (%)**	**Dispersion level**	**Amendment**	**Turbidity (NTU)**	**Dispersed clay (%)**	**Dispersion level**	**Amendment**
1†	327	0.06	Low	No	1901	0.37	Medium	Potential
2	3762	1.26	Very high	Yes	6633	2.23	Very high	Yes
3	1360	0.46	Medium	Potential	3707	1.24	Very high	Yes
4	3085	1.04	Very high	Yes	4058	1.36	Very high	Yes
5	612	0.21	Medium low	Potential	2209	0.74	High	Potential
6	1068	0.36	Medium	Potential	4154	1.39	Very high	Yes
7	110	0.04	Very low	No	977	0.33	Medium low	Potential
8	2376	0.80	High	Potential	5964	2.00	Very high	Yes
9	2715	0.91	High	Potential	5154	1.73	Very high	Yes
10	182	0.06	Very low	No	950	0.32	Medium low	Potential

†: the dispersed clay of soil 1 is calculated using c/τ =0.393.

Additionally, a strong relationship (R^2=0.734) is found between mechanical dispersed clay and two variables including EC and exchangeable sodium content (ESP × clay content) (Soil 1 has been excluded). Even higher correlation (R^2=0.771) is obtained when exchangeable dispersible content (EDP × clay content) has been used instead of exchangeable sodium content. Further, when SAR and CROSS values from soil solutions are considered as dispersive indices, strong and comparable relationships are found between mechanical dispersed clay and SAR (R^2=0.726) or CROSS (R^2=0.705) in conjunction with EC. Therefore, the dispersive indices of soils can be reasonably predicted where EC and dispersed clay content are known, at a resolution useful for farm management decisions.

3.5. Conclusions

This study clearly demonstrated that the turbidity of a dispersive clay solution with concentration beyond the capacity of a given turbidimeter is able to be determined by a diluting process. Subsequently, the colour and mean particle size of a colloidal solution has negligible effect on the linearity of turbidity between soils. Additionally, the relationship between turbidity and dispersed clay is strongly linear. A generalized equation was established to predict clay concentration from turbidity, although the single Oxisol soil investigated did not adhere well to this generalization. Alfisol (3) and Vertisol (6) soils had close coefficients with an average coefficient c/τ=0.677, subsequently used in the generalized equation.

By validating the relationship between turbidity and clay concentration, a user-friendly soil dispersion assessment chart has been developed. Application of the proposed chart will provide rapid diagnosis of soil dispersion severity, which can be further used as an index for soil management. Furthermore, where EC and clay content are known, it is possible to predict EDP (nee ESP) and CROSS (nee SAR) with accuracy suitable for practitioners.

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4. Ionicity of clay–cation bonds in relation to dispersive behaviour of magnesium and potassium soil clays as influenced by pH

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4.1. Abstract

Clay dispersive behaviour dynamics determine soil characteristics such as permeability, aggregate stability, crusting and erosion, and as a consequence crop productivity and geotechnical behaviour of infrastructure. Soil dispersion is highly influenced by the ionicity of clay-cation bonds, and has been shown to be related to the net negative charge and pH of the system. However, there is a paucity of work considering these factors together, especially in relation to K and Mg clays. This study investigated the effect of changing pH on dispersive behaviour of Mg and K homoionic clays of different clay mineralogy, in comparison to Ca and Na clays under equivalent pH condition, in relation to the ionicity concept. Three soils with distinct mineralogy were chosen (a Vertosol, Ferrosol and Chromosol) and their clay fraction obtained. These fractions were treated to become homoionic with regard to Na, K, Ca and Mg. Excess salts were removed by dialysis and pH was adjusted to 3, 4, 5, 6, 7, 8, 9, 10 and 11 for all clays, except Mg (pH range 3 to 7). Clay dispersion-flocculation dynamics were then investigated, measuring the net negative charge, pH, EC and turbidity. The effect of Mg on clay dispersion was shown to be greater than that of Ca, while the effect of K was less than Na, under similar pH conditions. Dispersive behaviour of Na, K, Mg and Ca homoionic clays was a function of ionicity of clay-cation bonds at equivalent pH, with the degree of clay dispersion explained by the pH, EC, ionicity, ζ-potential and mean particle size of the clay-cation system. A predictive model for dispersion was developed with its applicability and limitations discussed.

Keywords: clay dispersion; pH; exchangeable cations; zeta potential; clay mineralogy

4.2. Introduction

Understanding clay dispersive behaviour dynamics is essential to the determination of soil properties such as permeability, aggregate stability, crusting and erosion (Agassi et al., 1981; Curtin et al., 1994a; Frenkel et al., 1978; Hu et al., 2018a; Quirk, 2001; Shainberg and Levy, 2005). These properties have significant influence on crop production in cultivated areas and geotechnical behaviour under infrastructure. Recent investigations of soil structural stability have demonstrated that turbidity associated with dispersed clay is highly influenced by the ionicity — an indicator of covalent bonding — of clay-cation bonds (Marchuk and Rengasamy, 2011; Marchuk et al., 2013b). Therefore, further understanding the dynamics of dispersive systems and how ionicity relates to these is of value in moving towards prediction of dispersive behaviour on a soil-specific basis.

The ionicity concept of clay–cation bonds is based on: i) the fact that small higher charged cations have greater potential to polarize anions than lower charged and larger cations (Huheey et al., 1993); ii) the Misono softness parameter as an important factor in cation polarizability (Misono et al., 1967; Sposito, 1994; Sposito, 2008); and, iii) the assumption of clay as a large sized anion (Marchuk and Rengasamy, 2011). In essence, increasing the charge and/or the size of the clay anion will result in greater polarizability by the cation, at which point cations with greater charge, size and ionic potential will have greater capacity to form covalent bonds. In calculating the degree of ionic and covalent bonding, Marchuk and Rengasamy (2011) combined ionic potential and Misono softness parameters by multiplication into the covalency index, and then subtracted this from 1 to obtain the ionicity index. The ionicity indices of the cations decrease in the order Na(0.89)>K(0.86)>Mg(0.73)>Ca(0.67), whereby Ca has the greatest potential to form covalent bonds in the clay-cation system. Marchuk and Rengasamy (2011) found that the turbidity and mean particle sizes of Na, K, Mg and Ca homoionic clay suspensions were strongly correlated to the ionicity index. In comparison to the ionicity index, the correlation between clay dispersive behaviour and either ionic potential, or the Misono softness parameter, were poor. This showed the ionicity index as a better indicator than either the ionic potential or Misono softness parameter in explaining the clay dispersive behaviour (Marchuk and Rengasamy, 2011).

Na has traditionally been considered the major contributor to the deterioration of soil structural stability, which is reflected in the sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP) as indices indices in assessing and predicting soil structural decline (Amezketa, 1999; Rengasamy and Olsson, 1991; US Salinity Laboratory Staff, 1954).

However, research has suggested that Mg and K also affect soil structural stability (Arienzo et al., 2009; Emerson and Chi, 1977; Keren, 1991; Levy and Van Der Watt, 1990; Smiles, 2006; Zhang and Norton, 2002), which has led to the incorporation of Mg and K into new indices to replace SAR and ESP. The new indices included the cation ratio of soil stability (CROSS) (Rengasamy and Marchuk, 2011) and the exchangeable dispersive percentage (EDP) (Bennett et al., 2016a).

Chorom and Rengasamy (1995) studied the impacts of changing pH on dispersed clay and zeta potential (ζ) of Na- and Ca- saturated clay minerals, including kaolinite, bentonite and illite, and they found that pH affects clay dispersion primarily by changing the net negative charge on clay particles. The critical coagulation concentration of Na- and Ca-clay minerals is also pH dependent (Goldberg et al., 1991). A strong linear relationship was found between soil pH with both the dispersed clay (as determined by turbidity) and ζ-potential when soils were treated with CROSS solutions (Marchuk et al., 2013a). From this it is drawn that dispersion is specific to clay mineralogy and dependent on the charge density of the particle, as well as the pH, EC and CROSS of the soil solution. Therefore, we could expect that the effect of K and Mg on soil stability is influenced by ζ-potential, or the net negative charge on clays. However, there remains limited research on the net negative charge behaviour of K and Mg clays with different clay mineralogy and changing pH. The role of Mg is particularly contentious (Curtin et al., 1994b; Keren, 1991; US Salinity Laboratory Staff, 1954; Zhang and Norton, 2002), and has been demonstrated to both improve and worsen predictive capability of soil dispersion (Bennett et al., 2016a). Smith et al. (2015) reported that the flocculating ability of Mg, as compared to Ca, and the deleterious effect of K, as compared to Na, were optimisable. The authors explained this as a soil specific effect, but the reasoning for soil specificity was not investigated. On the basis of these differences, further investigating the role of pH on the net negative charge of K and Mg clays is required, within the context of ionicity, as these factors are likely to partially explain the soil-specific effect.

On the basis of the ionicity concept, we might expect K to behave similarly to Na, but with greater ζ-potential, and Mg to behave similarly to Ca, but with less ζ-potential. However, this requires investigation, specifically within the ionicity context in relation to soil stability. The following hypotheses were tested: 1) The effects of Mg on clay dispersion will be similar but greater than that of Ca, while the effects of K will be similar but less than Na, under same pH conditions; 2) The dispersive behaviour of Na, K, Mg and Ca homoionic clays is correlated with the ionicity indices of clay cation bonds at equivalent pH; and 3) the degree of clay dispersion is explained by the pH, EC, ionicity, ζ-potential and mean particle size of the clay-cation system. Therefore, the aim of this study was to investigate the effect of changing pH on dispersive behaviour of Mg and K homoionic clays of different clay mineralogy, and compare these dynamics to the behaviour of Na and Ca clays under equivalent pH conditions, in relation to the ionicity concept.

4.3. Materials and methods

4.3.1. Soil used

Three soils, a Ferrosol from Toowoomba (S1), a Vertosol from the Dalby region (S2) and a Chromosol from Adelaide (S3), all in Australia, were used in this study. Less than 2 µm clay fractions were acquired without any chemical treatments, using the method described by Churchman (2002). At this point, we acknowledge that clay suspension flocculation is not directly indicative of soil aggregation processes (Quirk, 2001). But this approach allows direct comparison with the initial work conducted by Chorom and Rengasamy (1995) and provides insight to the interactions occurring at the Stern Layer. The selected properties of these clays are presented in Table 4–1. The pH and electrical conductivity (EC) were measured at 1:10 clay/deionized water ratio. The organic carbon (OC) was determined according to Walkley and Black (1934). The exchangeable cations were determined according to the method 15A2 (Rayment and Lyons, 2011) and analysed on a NexION 300 ICP-MS and the effective cation exchange capacity (CEC_{eff}) was calculated as the sum of the exchangeable Na, K, Mg and Ca.

Table 4–1 Selected properties of soil clays

Clay ID	Soil classification	Soil depth (cm)	pH	EC (dS/m)	OC (%)	CEC ($cmol_c$/kg)
S1	Ferrosol	0–10	6.0	0.07	1.03	6.63
S2	Vertosol	0–10	7.5	0.17	1.02	66.84
S3	Chromosol	10–20	7.4	0.05	0.73	13.45

4.3.2. Preparation of homoionic clays

Homoionic clays were prepared by equilibrating with 1M NaCl, KCl, $MgCl_2$ or $CaCl_2$ solutions. The volume of solutions and the repetition time of the treatments were adjusted according to the clay mineralogy and type of salt (Bergaya et al., 2006a; Steudel and Emmerich, 2013). Excess electrolytes were removed using a modified dialysis method described by

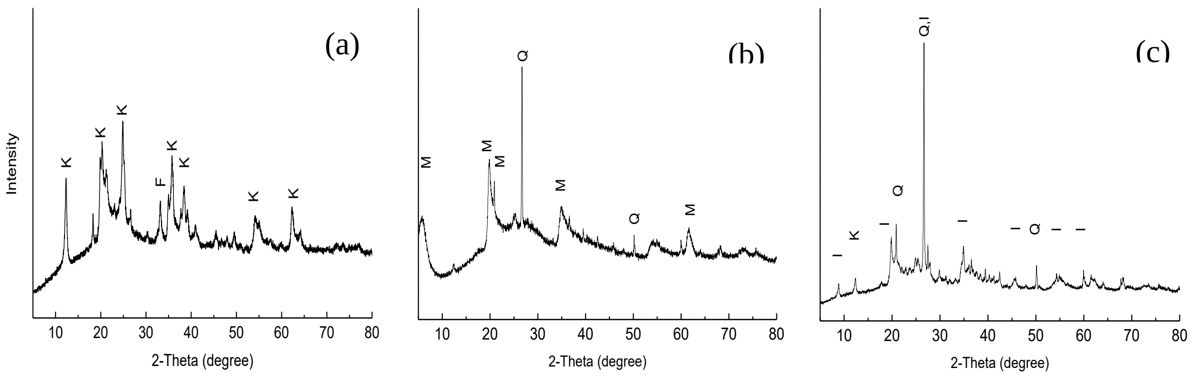
Churchman and Weissmann (1995) aiming that the EC of each homoionic clay reach <0.05 dS/m. The degree of homoionic cation suite within the clay was investigated via measuring the exchangeable cations using ICP-MS. The clay samples prepared by this method were subjected to hydrolysis resulting in the clay being 91–97% homoionic.

4.3.3. pH adjustment

Clay samples, each exactly 0.25 g of clay in 25 mL of water, were titrated manually to adjust pH to 3, 4, 5, 6, 7, 8, 9, 10 and 11 for all clays, using HCl to reduce the pH, or using the corresponding hydroxide solutions — *i.e.* NaOH for Na-clays, KOH for K-clays, $Mg(OH)_2$ for Mg-clays, $Ca(OH)_2$ for Ca-clays — to increase the pH (Chorom and Rengasamy, 1995). Due to the low solubility of $Mg(OH)_2$, which was used to increase the pH in Mg-clays, the highest pH value that was possible to obtain was pH 7 for kaolinite and illite clays and pH 8 for montmorillonite clays. The pH values were adjusted until stable desired pH values were obtained.

4.3.4. Clay mineralogical analysis using X-ray diffraction (XRD) and X-ray fluorescence analysis (XRF)

To confirm the clay mineralogical and chemical composition of three soil clays used, X-ray diffraction (XRD) and X-ray fluorescence (XRF) analysis was performed. The XRD analysis was performed on a Rigaku Smartlab X-ray diffractometer. Cu Kα radiation (λ=0.15406 nm) was generated at 40 kV and 35 mA and the scanning was from 5° to 80° 2θ at a speed of 5°/min, with step size of 0.02°. X-ray fluorescence (XRF) analysis was performed using an ARL 9800 X-ray spectrometer. The XRD patterns of three soil clays are given in Fig. 4–1 and the chemical composition from XRF analysis is shown in Table 4–2. Soil clay S1 was separated from a Ferrosol, and the major mineral was kaolinite $Al_2Si_2O_5(OH)_4$ with a small amount of ferric oxide (Fe_2O_3). Soil clay S2, derived from a Vertosol, was comprised mainly of montmorillonite $(Na_{0.07}K_{0.08}Ca_{0.13})(Si_{3.30}Al_{0.70})(Fe_{0.65}Al_{1.06}Mg_{0.28}Ti_{0.10})O_{10}(OH)_2 \cdot nH_2O$ and quartz. Soil clay S3, from a Chromosol, contained mostly illite with traces of kaolinite and quartz. The illite in S3 can be described as $(K_{0.33}Ca_{0.05})(Si_{3.10}Al_{0.90})(Fe_{0.62}Al_{1.03}Mg_{0.26}Ti_{0.13})O_{10}(OH)_2 \cdot nH_2O$, These data are in agreement with XRD analysis. The majority of the loss on ignition (LOI) value of the clays, as shown in Table 4–2, was attributed to the loss of structural water — the water retained within the clay quasicrystal.



K, kaolinite; F, ferric oxide; M, montmorillonite; I, illite; Q, quartz.

Fig. 4–1 Comparison of XRD patterns between clays (a) Kaolinite-based soil clay S1 (b) Montmorillonite-based soil clay S2 (c) Illite-based soil clay S3.

Table 4–2 Chemical composition analysis of clays (% wt)

Clay ID	**Main Mineral**	SiO_2	Al_2O_3	Fe_2O_3	*CaO*	*MgO*	SO_3	TiO_2	K_2O	Na_2O	P_2O_5	*LOI*
S1	Kaolinite	32.73	32.39	13.44	0.11	0.24	0.15	2.61	–	0.06	0.46	17.36
S2	Montmorillonite	44.85	17.60	10.11	1.40	2.23	0.07	1.55	0.76	0.44	0.19	20.39
S3	Illite	47.34	21.32	9.88	0.53	2.11	0.11	2.05	3.07	0.31	0.26	12.73

4.3.5. Measurements of dispersed clay percentage, ζ-potential and mean particle size

The percentage of dispersed clay was calculated following the measurements of clay dispersion as turbidity in NTU on each clay sample, as described in Zhu et al (2016), using a Hach Turbidimeter 2100N.

Three separate ζ-potential measurements were performed on each clay sample using zeta cells on a Malvern Zetasizer Nano-ZS analyser. The ζ-potential was calculated automatically for each clay sample as a mean of 100 runs by Zetasizer Software v7.11.

The same Malvern Zetasizer Nano-ZS analyser and software were used to measure mean clay particle sizes at 25°C by dynamic light scattering spectroscopy using particle size cells. The mean particle size was calculated after three measurements, and each measurement was averaged over 13 individual runs.

4.3.6. Statistical analyses

Descriptive statistics were utilised to investigate all data. The average value of the percentage of dispersed clay, ζ-potential and mean particle size were plotted with standard deviation as error bar. A one-way ANOVA analysis was performed to determine if the dispersed clay, ζ-potential and mean particle size varied significant between Na, K, Mg and Ca clays within same pH. To explore the relationships for dispersed clay against ionicity index, ζ-potential, mean particle size and pH, stepwise regression analysis with both forward and backward propagation were conducted. The regression equations were given at 95% confidence limits, with the coefficient of determination (R^2), adjusted R^2, predicted R^2 and Mallow C_p provided to assess the variation explained, potential over parameterisation, capability to predict new data, and precision of the model, respectively.

4.4. Results

4.4.1. Behaviour of homoionic clays prior to pH adjustment

The results in Fig. 4–2 showed differing dispersion between homoionic clays before any pH adjustment, with the dispersed clay percentage in the order of Na>K>Mg>Ca, regardless of soil-clay dominant mineral type. Mg clays had 7.8–25.5% more dispersed clay than Ca clays, and K clays had 17.5–20.3% less dispersed clay than that of Na clays, depending on clay mineralogy. The values of pH, ζ-potential, dispersed clay and mean particle size of Na, K, Mg and Ca treated clays, before the pH changes, are presented in Table 4–3. The electrophoretic mobility (ζ-potential) of dispersed clay indicated the changes in net charge. In general, the ζ-potential and mean particle size of homoionic clay was in the order of Na<K<Mg<Ca at pH control.

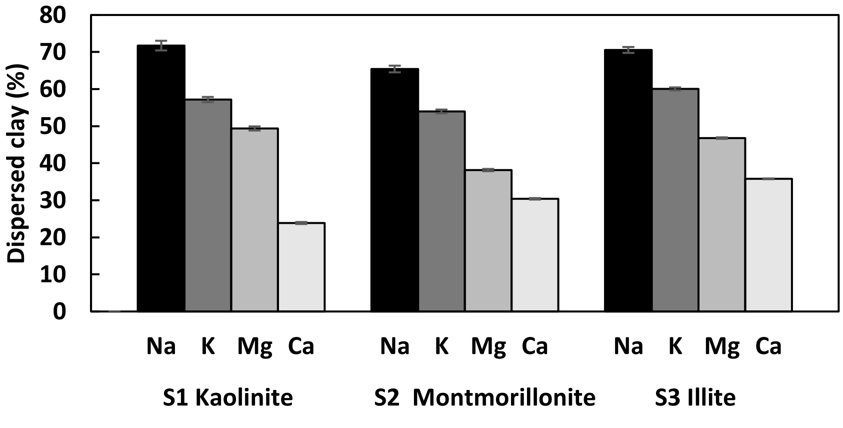


Fig. 4–2 Comparison between the percent of dispersed clay of the treated clays prior to pH manipulation

Table 4–3 Original pH, ζ-potential, dispersed clay percentage and particle size of clays before altering pH

Type of clay	Saturated cations	pH	Dispersed clay %	ζ-potential mV	Mean particle size nm
S1 Kaolinite	Na	7.4	71.74	-51.0	531.8
	K	6.9	57.18	-50.6	550.2
	Mg	6.4	49.38	-27.0	559.0
	Ca	6.5	23.87	-26.2	588.0
S2 Montmorillonite	Na	8.1	65.43	-53.7	243.3
	K	7.7	53.98	-51.5	351.7
	Mg	7.3	38.16	-21.9	454.2
	Ca	7.4	30.40	-20.4	513.1
S3 Illite	Na	7.5	70.56	-57.2	318.7
	K	6.8	60.06	-54.9	390.0
	Mg	6.6	46.79	-25.0	440.8
	Ca	6.8	35.80	-23.3	585.7

4.4.2. Behaviour of homoionic clays with changing pH

The behaviour of the homoionic clays occurring with the change of pH is discussed by dominant mineralogy in the following section. The visual changes in dispersive behaviour of Na, K, Mg, Ca soil clays at pH 3 to pH 11 are presented in Appendix A.1 as useful supporting information for confirmation of flocculation at a given pH.

4.4.2.1. Kaolinite dominant clay

The values of dispersed clay, ζ-potential and mean particle size of homoionic kaolinite (S1) soil clays are plotted in Fig. 4–3. When the percentage of dispersed clay was less than 5, the clay suspension system was classified as flocculation (Zhu et al., 2019). Mg and Ca kaolinite clays flocculated at pH 3 to 6, but showed 29% dispersion for Ca clay and 41% for Mg clay at pH 7, where pH 7 was the highest pH value reported for Mg-S1 clay in this study. Mg-S1 clays carried a net positive charge at pH 3, as indicated by ζ-potential of 2.7 mV. Above pH 4, Mg-S1 platelet carried a net negative charge. The ζ-potential of Mg-S1 was negatively greater than that of Ca-S1 clays with the difference between 1.1–2.6 mV depending on pH value. At each pH reading, the mean particle size of Mg clays was smaller than that of Ca clays. At pH>7, Ca-S1 clay tended to flocculate. The ζ-potential and mean particle size of Ca-S1 increased when pH was above 7.

The K and Na kaolinite (S1) clays flocculated at pH 3, 4 and 5, but both showed dispersion higher than 30 % at the rest of the measured pH values. At any given pH the dispersion in K-S1 clays was lower than for Na-S1 clays, with the highest difference of 20% at pH 6 and only 2% difference at pH 11. When pH increased from 3 to 7, the ζ-potential of K-S1 clay decreased sharply as shown in Fig. 4–3(b) from 2.5 to -50.8 mV. At pH 8 to 11, K-S1 clays had comparable ζ-potential values to that at pH 7. Noticeably, the ζ-potential of Na-S1 clay was slightly higher than that of K-S1 clay. The mean particle size of K-S1 clays decreased dramatically when the pH increased from 3 to 11. Na clays had a similar trend to K clays but with a smaller mean particle size at the same condition.

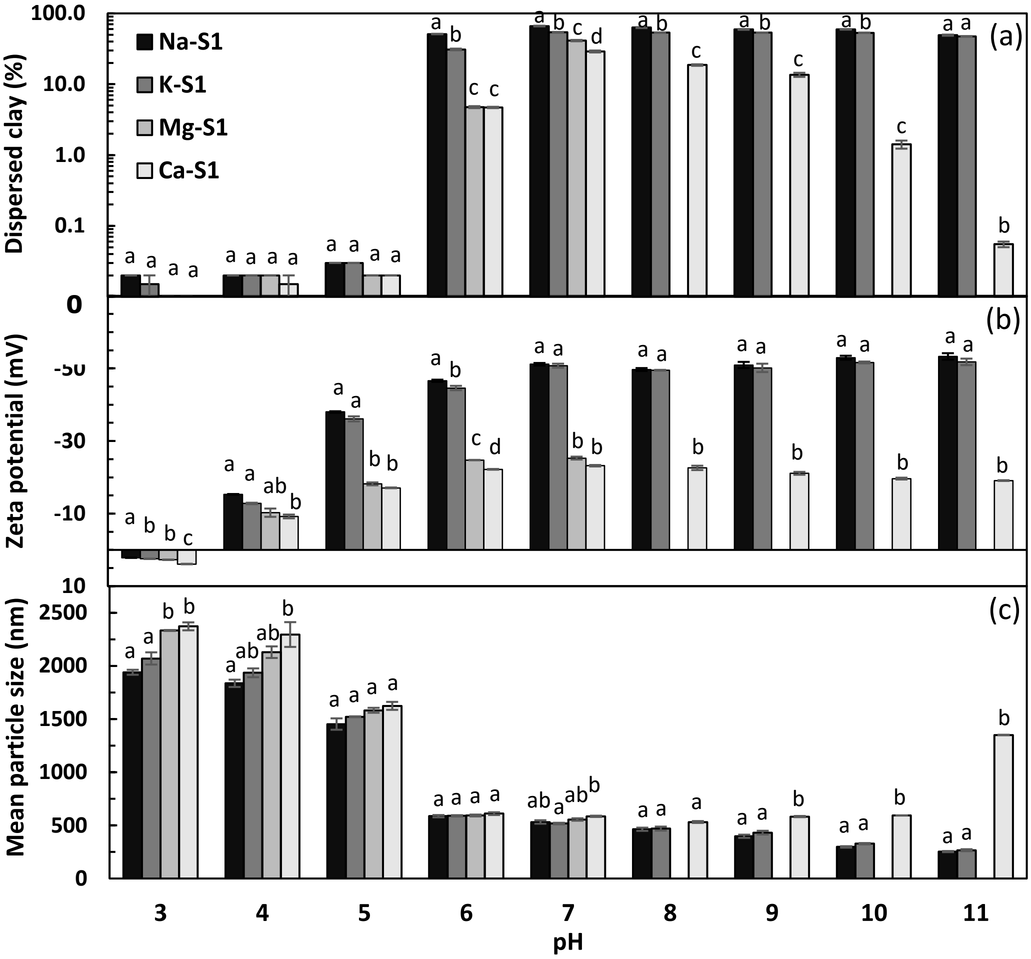


Fig. 4–3 The dispersed clay in log. scale (a), ζ-potential (b) and mean particle size (c) of Na, K, Mg and Ca homoionic kaolinite soil clay (S1) at varying pH. The bars represent the standard error and the lowercase letters represent significant differences between Na, K, Mg and Ca clays within pH.

4.4.2.2. *Montmorillonite dominant clay*

Mg and Ca montmorillonite (S2) clays flocculated at pH 3–6 but dispersed at pH 7 and 8 (Fig. 4–4), which behave similarly to Mg- and Ca- kaolinite (S1) clays The greatest ζ-potential for Mg-S2 was found at pH 3 (-10.8 mV), which was much lower than that of Mg-S1 at same pH reading. As pH approached 8, ζ-potential of Mg-S2 gradually decreased to -20.7 mV. The mean particle size of Mg-S2 was smaller than that of Ca-S2 at similar condition. When the pH was ≥7, Ca-S2 tended to flocculate with increased ζ-potential from -18.6 mV at pH 7 to -15.5 mV at pH 11. This was associated with a mean particle size increased from 541 nm at pH 7 to 913 nm at pH 11.

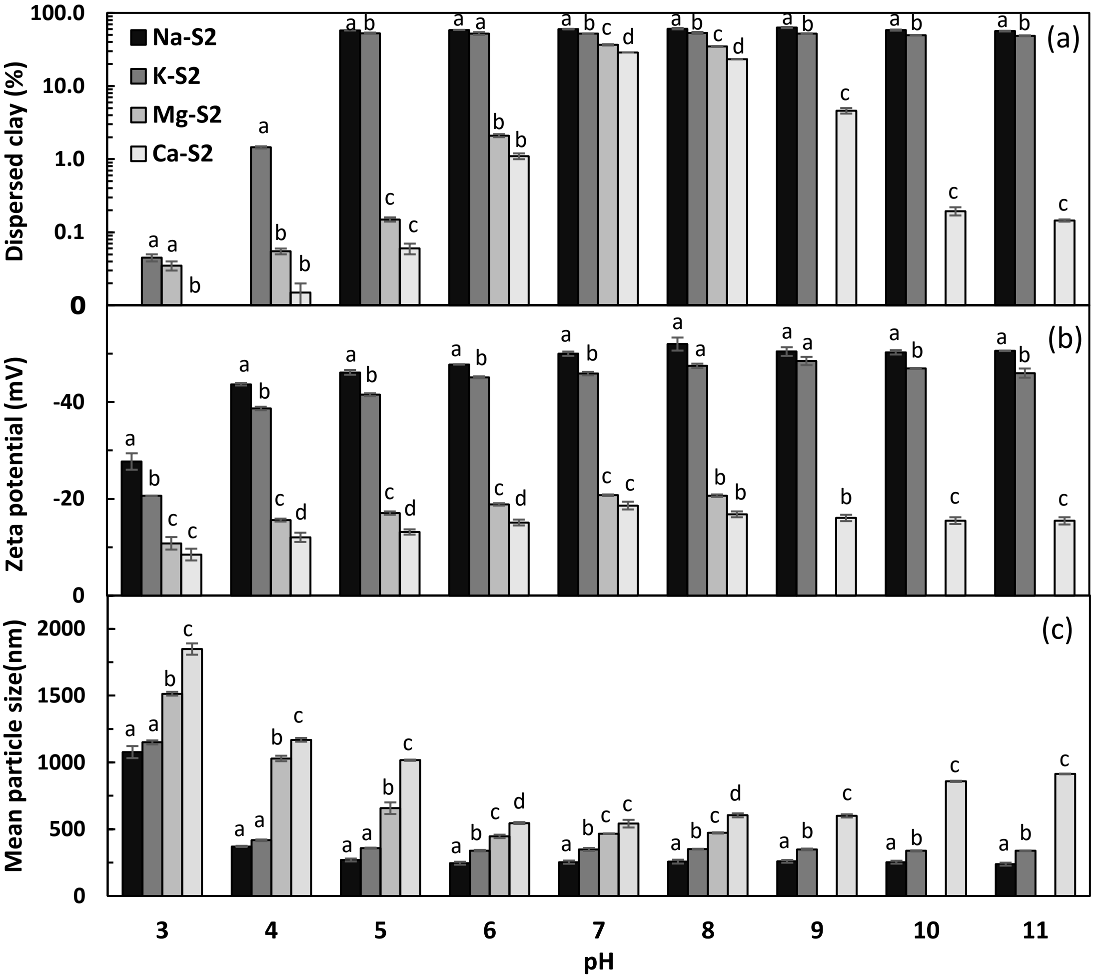


Fig. 4–4 The dispersed clay in log. scale (a), ζ-potential (b) and mean particle size (c) of Na, K, Mg and Ca homoionic montmorillonite soil clay (S2) at varying pH. Partially flocculation was observed in Na montmorillonite clays at pH 3 and pH 4 without given dispersed clay (%) data. The bars represent the standard error and the lowercase letters represent significant differences between Na, K, Mg and Ca, clays within pH.

K-S2 flocculated at pH≤4, whereas partial flocculation was observed in Na-S2 at the same pH condition. Considerable dispersion, above 50%, was observed for both K- and Na-S2 clays, starting at pH 5. The greatest ζ-potential and mean particle size for K- and Na-S2 clays was observed at pH 3; increasing pH resulted in a decrease of both parameters, which behave similarly to Na- and K- kaolinite (S1) clays. At each pH reading, K-S2 had greater ζ-potential and mean particle size than Na-S2 clay.

4.4.2.3. *Illite dominant clay*

For Mg- and Ca- illitic (S3) clay, flocculation took place at pH 3 and 4, which was unlike Mg- and Ca- variants of both kaolinite and montmorillonite clays, where flocculation was observed at pH≤6. Appreciable amounts of dispersed clays existed from pH 5 for Ca and Mg dominant clays; *i.e.* 44.7% dispersed clay for Mg-S3 clay and 28.1% dispersed clay for Ca-S3 clay. Mg-S3 had similar dispersed clay percentage at pH 6 and pH 7 to that at pH 5, which was greater than that of Ca-S3 at all times. There was no significant difference between Mg- and Ca-S3 clays in terms of ζ-potential with pH. However, the ζ-potential of Mg-S3 clay was constantly smaller than that of Ca clays at each pH. The mean particle size of Mg-S3 clay was smaller than that of Ca clays at all pHs measured. A comparable amount of dispersed clay (33.7%), for Ca-S3 as compared to lower pH, was observed even when pH increased to 10, while flocculation occurred at pH 11.

K-S3 and Na-S3 clay flocculated only at pH 3. When the pH was ≥4, more than 45% dispersed K-S3 clay was observed; by comparison, Na-S3 had more than 65% dispersed clay. K-S3 has lower dispersed clay than Na-S3 at all similar pH conditions. At pH 4–11, no significant difference between K- and Na-S3 clays was found in terms of the ζ-potential with pH, where the ζ-potential of K-S3 was always lower than -46.7 mV, and the ζ-potential of Na-S3 always lower than -50.0 mV. In general, the mean particle size of K-S3 and Na-S3 decreased as pH increased, and at each pH reading, Na-S3 consistently had smaller ζ-potential and mean particle size than K-S3 clay.

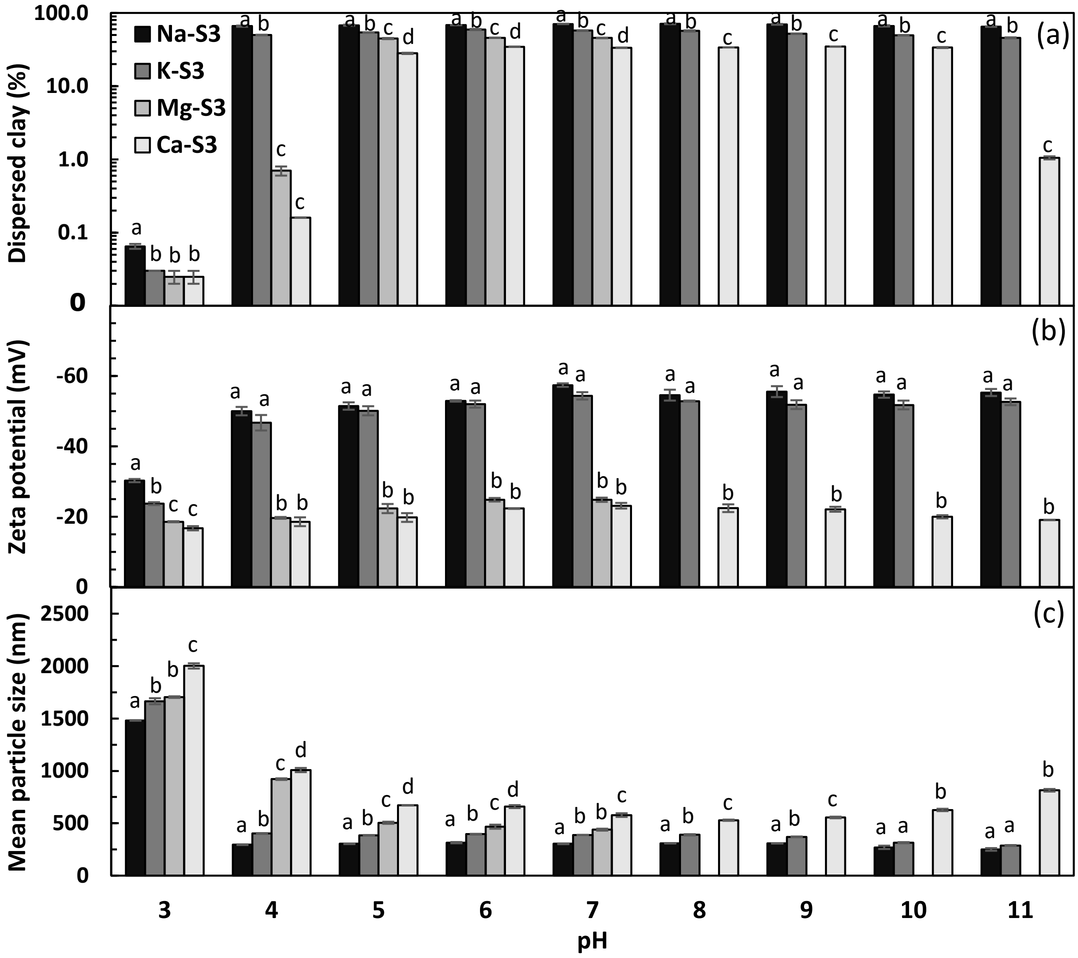


Fig. 4–5 The dispersed clay in log. scale (a), ζ-potential (b) and mean particle size (c) of Na, K, Mg and Ca homoionic illite soil clay (S3) at varying pH. The bars represent the standard error and the lowercase letters represent significant differences between Na, K, Mg and Ca, clays within pH.

4.4.3. Clay suspension electrolyte concentration

The EC of each clay suspension was measured for inclusion in dispersive clay relationships with multiple factors and is presented in Table 4–4 below. The EC for each homoionic soil clays was lowest at neutral pH and increased toward more acid and more alkaline suspension solutions. This was a function for acid addition for acid solutions, and alkali addition for alkaline solution. The greatest EC for each homoionic clay was found at the lowest pH, *i.e.* pH 3.

Table 4–4 The measured EC (dS/m) of soil clays at corresponding pH

pH	S1				S2				S3			
	Na	**K**	**Mg**	**Ca**	**Na**	**K**	**Mg**	**Ca**	**Na**	**K**	**Mg**	**Ca**
3	0.55	0.58	0.72	0.65	1.69	1.35	1.19	1.09	0.59	0.56	0.54	0.55
4	0.13	0.13	0.13	0.14	0.90	0.58	0.39	0.42	0.18	0.15	0.13	0.14
5	0.06	0.07	0.05	0.05	0.55	0.32	0.20	0.20	0.11	0.08	0.06	0.05
6	0.05	0.04	0.02	0.02	0.32	0.22	0.12	0.12	0.07	0.04	0.02	0.02
7	0.02	0.02	0.02	0.02	0.19	0.14	0.06	0.06	0.03	0.03	0.04	0.02
8	0.06	0.05		0.04	0.10	0.12	0.06	0.09	0.05	0.05		0.04
9	0.09	0.08		0.04	0.14	0.16		0.11	0.07	0.08		0.04
10	0.11	0.15		0.07	0.22	0.35		0.16	0.10	0.13		0.07
11	0.46	0.55		0.13	0.42	0.78		0.21	0.25	0.28		0.13

4.4.4. Dispersed clay relationships

The role of ionicity of clay–cation bonds in explaining dispersed clay (%) and ζ-potential for homoionic clay suspensions was investigated with the results presented in Table 4–5. There was no significant correlation for the data when treated as a single data-set, or by soil, meaning that both the mineralogy and the pH affected the relationship between dispersed clay and the ionicity index. When dispersed clay was correlated with ionicity at a given pH for a given mineralogy it was found to be highly correlated, explaining >86% of variation, and was highly significant ($p<0.0001$) for all instances. Strong relationships ($R^2>0.94$) were also found between ζ-potential and ionicity for a certain pH and clay mineralogy.

In order to explore generalised relationships for dispersed clay (%) against soil characteristics, step-wise regression was undertaken using the pH (explanatory variable) and EC (varied by necessity of treatment), as well as the ionicity index, given the results in Table 4–5, resulting in Equation 4.1. In testing the hypothesis that dispersed clay is related to the ionicity index the mean particle size was added as a factor, with the net negative charge (ζ-potential) also added, resulting Equation 4.2.

Table 4–5 Relationship between the ionicity index (I) and zeta potential (ζ) as well as the dispersed clay percentage (D) of homoionic clays at pH control (without pH adjustment), pH 6, pH 7 and pH 8

Soil clay ID	*pH*	*Regression equation*	R^2	*P value*
S1	Control	$D=178.1I-89.7$	0.86	<0.0001
	6	$D=202.6I-136.7$	0.89	<0.0001
	7	$D=149.8I-70.4$	0.95	<0.0001
	8	$D=195.4I-112.5$	0.99	<0.0001
S2	Control	$D=147.6I-69.3$	0.97	<0.0001
	6	$D=290.2I-200.1$	0.95	<0.0001
	7	$D=135.7I-62.4$	0.99	<0.0001
	8	$D=163.6I-85.3$	0.99	<0.0001
S3	Control	$D=142.7I-59.0$	0.97	<0.0001
	6	$D=140.4I-58.6$	0.98	<0.0001
	7	$D=148.0I-64.8$	0.94	<0.0001
	8	$D=152.3I-68.9$	0.93	<0.0001
S1	Control	$\zeta= -129.7I+63.5$	0.94	<0.0001
	6	$\zeta= -121.0I+60.8$	0.97	<0.0001
	7	$\zeta= -144.2I+76.0$	0.96	<0.0001
	8	$\zeta= -129.7I+64.0$	0.99	<0.0001
S2	Control	$\zeta= -169.8I+95.8$	0.95	<0.0001
	6	$\zeta= -161.4I+95.4$	0.97	<0.0001
	7	$\zeta= -154.1I+85.6$	0.97	<0.0001
	8	$\zeta= -170.5I+100.0$	0.98	<0.0001
S3	Control	$\zeta= -172.4I+95.7$	0.96	<0.0001
	6	$\zeta= -156.5I+85.3$	0.96	<0.0001
	7	$\zeta= -172.9I+96.2$	0.96	<0.0001
	8	$\zeta= -151.2I+78.7$	0.99	<0.0001

Dispersed clay (%), D, was explained by the pH, EC (C) and the ionicity index (I) as follows:

$$D = 172I + 3.27pH - 25.7C - 121.3 \qquad \text{Eq. 4.1}$$

while net negative charge (ζ), mean particle size (P) and EC were shown to explain dispersed clay (%) as:

$$D = -0.777\zeta - 0.0138P + 38I - 7.2C - 12.122 \qquad \text{Eq. 4.2}$$

The statistics for Equation 4.1 and 4.2 are given in Table 4–6. Both equations explain the majority of variation in dispersed clay as a function of their factors. However, Equation 4.2 is clearly superior to Equation 4.1. That said, the efficacy of Equation 4.2 can only be considered as reasonable. While neither model is over parameterised ($R^2 \approx R^2_{ADJ}$), with both models having reasonable predictive capacity (R^2_{PRED}) and precision ($C_p \approx$ the number of model parameters), there was substantial deviation of predicted results from observed results within the models (Table 4–6). Equation 4.2 resulted in 92% of data being within +/-15% dispersed clay, as compared to the true value, and 42% of data varying by less than +/-5% dispersed clay; for Equation 1, these values were as compared to 75 and 29% of data being within the ±15% and

±5%, respectively(Table 4–6). This indicates that neither equation provides exceptional predictive capacity, but that Equation 2 is reasonable. Both equations also provided low confidence in predicting suspension conditions where the dispersed clay percentage was <12%. Below this concentration, the suspension system was unstable (i.e. clay flocs formed rapidly), indicating that the system was actually better explained by a two phase model (flocculated and unstable suspension; dispersed and stable suspension), which should not be considered surprising. Separating the data into these phases did not improve predictive capacity, but <12% dispersed clay was clearly delineated as the boundary condition in terms of all regression models explored, with the caveat this is for the observed data in this work. It is cautioned against the use of these equations for aggregated soil systems, as these results are based on clay suspensions; the intention of the results being to facilitate mechanistic investigation.

Table 4–6 Statistical characteristics pertaining to Equation 4.1 and 4.2 deviation from validation data. Dev. Refers to deviation of the predicted results from the true result observation; R^2, explains the variation described by the model; R^2_{ADJ} is the adjusted R^2; R^2_{PRED} is the predicted R^2; C_p is Mallow's measure of precision; N_{Dev} is the number of observation pertaining to the deviation data; and N is the total number of observations used in the construction and subsequent statistical assessment of model efficacy.

Statistic	**Unit**	**Eq. 4.1**	**Eq. 4.2**
Min	%	0.03	0.09
Max	%	26.97	20.83
Mean	%	9.98	6.94
Dev.<5%	%	29	42
Dev.<10%	%	54	71
Dev.<15%	%	75	92
R^2	%	61	79
R^2_{ADJ}	%	61	78
R^2_{PRED}	%	58	77
C_p	%	4.0	4.2
N_{Dev}		118	118
N		190	190

4.5. Discussion

4.5.1. The effect of magnesium and potassium on clay dispersion behaviour at varying pH

The general trend in terms of the dispersive behaviour of homoionic clays can be found: 1) the dispersed clay (%) was in the order: Ca<Mg<K<Na; 2) the ζ-potential of homoionic clays was in the order of Ca>Mg>K>Na; and, 3) the mean particle size of homoionic clays was in the order: Ca>Mg>K>Na. These sequences occurred at the equivalent pH observation, irrespective of clay type. These findings support parts of the first hypothesis: the effects of Mg on clay dispersion are greater than that of Ca, while the effects of K are less than Na, under similar pH conditions.

Our results showed that Mg clays were in very close agreement with Ca clay behaviour. For the same clay mineralogy, Mg and Ca clays had same critical pH value that distinguished flocculation and dispersion at low pH. At neutral pH, Mg clays had slight higher dispersed clay (%) than Ca clays under similar conditions. The greatest pH values for magnesic clay were pH 7, 7, and 8 for Mg-S1, Mg-S2, and Mg-S3, respectively, due to the low solubility of $Mg(OH)_2$. While, at high pH, Ca clays tended to flocculate regardless of clay types with increasing ζ-potential and mean particle size. The flocculation tendency of Ca clays at high pH could be related to the increased electrolyte concentration (Table 4–4) in the suspension from the addition of alkali solution and/or mineral dissolution. Furthermore, clay particles are flocculated by charge reduction due to cementation or coating by the formation of $CaCO_3$ in Ca-clays suspension at the exposure to atmospheric CO_2 (Chorom and Rengasamy, 1995). When Mg cations were initially present in soil/soil water, an increase in pH upon alkalization could result in the precipitation of magnesium hydroxide. $Mg(OH)_2$ precipitation begins at approximately pH 9.5, becoming significant above 10.5, and essentially completed at pH=11-11.5 (Semerjian and Ayoub, 2003). The resulting $Mg(OH)_2$ was a gelatinous precipitate with a large adsorptive surface area and a positive superficial charge, which was found to serve as an efficient coagulant and flocculent aid (Semerjian and Ayoub, 2003). Therefore, under high pH conditions, we assume that Mg should behave in a similar fashion to Ca, and tend to flocculate clay suspensions.

The results in this study further showed that Mg clays were in very close agreement with Ca clay behaviour, albeit with a net negative charge consistently more negative than Ca (greater electrophoretic mobility). The Ca system was conducive to flocculation conditions with ζ-potential >-30 mV (Molina, 2013). Our results demonstrate that, while Mg-clay<Ca-clay in terms of ζ-potential, conditions for an unstable clay dispersion (prone to flocculation) were always obtained with ζ-potential <-30 mV. This clearly suggests that the role of Mg is similar to the role of Ca, irrespective of mineralogy, and that it has a flocculative effect rather than a dispersive effect, allowing us to accept the first hypothesis with regard to Mg.

K kaolinite and illite clays completely flocculated within the same pH ranges where Na saturated clay flocculated. K montmorillonite flocculated at pH≤4 while partial flocculation was observed in Na montmorillonite clay at the same pH range. The ζ-potential of K clays was very close but slightly greater than Na clays at each pH reading, regardless of clay mineralogy, which was consistent with less dispersion in K clays. Where the Na-clay system had ζ-potential <-30 mV (stable clay dispersion), the K-clay had ζ-potential <-30 mV, indicating that the K clay behaviour was largely in line with Na clay. Additionally, the mean particle size of K clays had close but higher mean particle size than Na clays under equivalent conditions. The general results confirmed that K had similar dynamics with pH as compared to Na, but induced less dispersion, which was in agreement with the general hypotheses raised by Rengasamy and Marchuk (2011) and in this work.

The dispersive behaviour of monovalent clays was distinct from divalent clays, particularly at high pH. As noted, Ca clays tended to flocculate, while monovalent clays maintained high degree of dispersion, *e.g.* K-S3 52.1%, 49.6% and 45.7% at pH 9, pH 10 and pH 11. The monovalent clays were highly dispersive because of the strong negative charge, as the addition of OH^- in solution led to more OH^- ions absorbed by mineral surfaces (Chorom and Rengasamy, 1995). This can be supported by comparable ζ-potential to that at neutral pH, in spite of the increased EC at high pH as shown in Table 4–4. Moreover, when pH≥9, the mean particle size of monovalent saturated soil clay decreased. This could also be attributed to the increased pH which decomposed the bonding between organic matter and clay particles in soil clays as a result of decreasing average mean particle sizes (Marchuk et al., 2013a). In terms of the roles of K and Mg in clay dispersion, we are able to accept our first hypothesis that the effects of Mg on clay dispersion will be similar but greater than that of Ca, while the effects of K will be close but less than Na, under similar pH conditions.

4.5.2. Application of the ionicity concept in explaining specific clay dispersive behaviour

In dilute electrolytes, the separation distance of some clay particles often follows DLVO (Derjaguin, Landau, Verwey and Overbeek) theoretical prediction (Hartley et al., 1997; Quirk and Marcelja, 1997). However, the DLVO theory has its limitations, which predicts that the double layer interactions depend only on the valence of the electrolyte ions, regardless of their nature (Hu et al., 2018b; Karraker and Radke, 2002; Manciu and Ruckenstein, 2003; Pashley and Quirk, 1984). The different behaviour between Mg and Ca clays, and between K and Na clays, apparently cannot be explained by DLVO theory. Strong correlations ($0.86<R^2<0.99$) were observed between ionicity indices of the four cations and the percentage of dispersed clay at the control (without pH adjustment), pH 6, pH 7 and pH 8 as shown in Table 4–5. Hence, the difference between Mg and Ca clays, and between K and Na clays can be explained by their differences in the degree of ionicity and subsequent strength of clay-cation bonds. The results in our study provide further confirmation that clay-cation bonds are a mixture of covalent and ionic bonds, where the net ionicity of a clay-cation bond determined how water reacted with clays and the degree of hydration (Marchuk and Rengasamy, 2011; Rengasamy et al., 2016). While our work is conducted in clay suspensions (i.e. not directly equivalent to an aggregated soil system), the mechanism of increasing covalency of clay-cation bonds will lead to enhanced potential for aggregation of clay particles, and/or retention of aggregation under some adverse conditions. This was reflected by the mean particle sizes of homoionic clays at each pH value being in the sequence of Na<K<Mg<Ca. Therefore, it is demonstrated that the ionicity approach to explaining soil stability under dynamic conditions will be useful in informing predictive models.

Even though the ionicity index had high correlation to clay dispersive behaviour, the gradient of the relationship between ionicity and clay dispersion parameters varied substantially (Table 4–5). This variability in coefficients suggested potential for other factors, or a specific effect. First, while the clay suspensions were considered homoionic, it was impossible to remove all other ions from the system. This, and the fact homoionic systems would not be expected in a natural soil environment, highlights that there is merit in developing an ionicity index approximation for mixed ion systems. Secondly, the deviation in gradient may be partly related to the existence of iron oxide and organic matter within the colloidal system (Goldberg and Glaubig, 1987; Goldberg et al., 1990; Marchuk et al., 2013a), and the fact that clay structure varies in terms of different clay mineralogy (Brigatti et al., 2006), with natural soils not having a consistent mineralogy, but rather a possible dominant mineral and mixed mineral suite. As the mineral suite changes, the charge density and its distribution will also vary, even within the same dominant clay mineralogy (Lagaly, 1981; Saka and Güler, 2006). Therefore, we suggest that organic matter, sesquioxides and clay source are also important factors explaining specific clay dispersive behaviour. On such basis, further investigation is required: 1) the effect of variations within a clay mineral class is needed to establish the application of the ionicity concept; and 2) an ionicity index approximation for a mixed ionic system required to determine the specific effect. Despite these variations, our results confirm the second hypothesis that at equivalent pH the dispersive behaviour of Na, K, Mg and Ca homoionic clays is correlated with the ionicity indices of clay cation bonds.

4.5.3. Predicting dispersive behaviour of clay suspensions

This study demonstrates that the degree of clay dispersion is explained by the pH, EC, ionicity, ζ-potential and mean particle size of the clay-cation system, but not as a single equation. Chorom and Rengasamy (1995) demonstrated that solution pH and EC had distinct effect on the level of stability within a clay suspension, while Marchuk and Rengasamy (2011) showed that clay suspension dispersion was related to ionicity. Hence, it was expected that a generalised relationship would exist between pH, EC and ionicity in explaining clay suspension dispersion, as found in Equation 1. The subsequent incorporation of net negative charge and particle size resulted in pH being dropped from the model and substantial improvement in the predictability of new results. The removal of pH with the introduction of net negative charge is explained by the fact that net negative charge varies as a result of change in pH, as described by Chorom and Rengasamy (1995), meaning that net negative charge inclusion makes the pH term redundant. Interestingly, we see that EC is not dropped, despite the relationship to net negative charge: when the EC increased, the double layer is compressed, resulting in a smaller net negative charge (Brown et al., 2016; Chorom and Rengasamy, 1995). We suggest that this is because the more dominant mechanism of EC effect is via osmotic potential, as described by Quirk (2001). Hence, the osmotic effect of EC on clay particle dispersion appears to be more important than the effect of EC on net negative charge.

From the data obtained from the three distinctly different dominant soil mineralogy, it was seen that a general boundary condition exists between 5 and 12% dispersed clay in terms of the predictive capability of Equations 1 and 2, suggesting that the dispersion-flocculation condition is a two phase model. The predictive models could not provide any reasonable confidence in predicting dispersed clay content below 12.7%. The two phase model should be expected given the classical work of Quirk and Schofield (1955) who demonstrated that dispersion-flocculation and aggregation-dispersion thresholds were clear, but occurred at different characteristic conditions (i.e. flocculation and aggregation are not equivalent phenomena). The results for dispersed clay and the flocculation conditions on a dominant soil-clay-mineral basis are supported by the depiction in Appendix A.1, and quantified in terms of the dispersed clay extent, net negative charge, and mean particle charge in our results. In general terms, flocculation occurred within acid systems, but was also explained by the changes in EC (Equation 1 and 2), while for divalent homoionic systems alkaline conditions approach flocculation conditions also. The specific occurrence of these appears to be explained by mineralogy, but requires further quantification beyond the use of a single soil-clay-dominant sample. For example, at pH≤5, kaolinite soil clay (S1) exhibited a greater propensity to flocculate and was less dependent on cation effect than montmorillonite (S2) and illite (S3) clays. In other words, the effect of the H^+ proton (H_3O^+) in montmorillonite and illite was not as strong as in kaolinite and the exchangeable cations (Mg^{2+}, K^+, Na^+ and Ca^{2+}) played a more important role. Treating the flocculated suspensions as a separate data set and utilising the same predictive factors (i.e. pH, EC, ionicity, ζ-potential, and mean particle size) resulted in a model with extremely low predictive capability with low precision and <20% of data variation explained by the included factors. This supports that the boundary condition is determined by a factor external to those measured, with the soil-clay-mineral suite the mostly likely explanatory variable. Therefore, we suggest that there is requirement for greater soil mineral suite investigation in terms of controlling the dispersive extent. It would be most advantageous if this were quantified, rather than included as qualitative XRD analysis.

4.5.4. Mineralogical observations

For dispersed clay suspensions, the ζ-potential at each pH reading changed in response to clay mineralogy and was integral in explaining the actual dispersive extent. Distinct difference between kaolinite and montmorillonite were observed at low pH, which could be explained by the different clay structures and their charge changing when interacting with acid solutions. The alumina octahedral layer of kaolinite was positively charged at pH<6 (Gupta and Miller, 2010), while the silica tetrahedral layer was always negatively charged, though its magnitude was pH-dependent possibly due to broken bonds on the basal planes and/or hydrolysis of siloxane bonds (Zhou and Gunter, 1992). The surface charge of kaolinite crystal edge was positive at pH<4.5. Unlike kaolinite, montmorillonite possesses large permanent negative charge and negligible variable charge (Tombácz and Szekeres, 2004; Weil and Brady, 2016). Thus, at low pH, the positively charged surface of aluminium layer of kaolinite and its highly exposed edge surface area with positive charge had less net negative charge than that of montmorillonite. This was supported in our work whereby the ζ-potential of each homoionic montmorillonite was more negative than kaolinite at pH≤5. It is deduced that determining clay mineralogical contributions and dynamics associated with surface and edge charge will be important in the development of more precise predictive models and the associate threshold conditions.

The results from this study showed that homoionic illite clays were more dispersive than kaolinite and montmorillonite clays, with each treated illite clay having greater percentage of dispersed clay than the corresponding montmorillonite and kaolinite clays at equivalent treatment. In addition, the treated illite clay showed notable dispersion in a wider pH range than that of montmorillonite and kaolinite. For example, Ca illite clay had notable dispersion from pH 5 to pH 10, while Ca-kaolinite and Ca-montmorillonite showed visible dispersion only within the range of pH 7 to pH 9. The results in this study are in line with reports that illitic red-brown earths are susceptible to dispersion even at SAR<3 and under weak mechanical forces (Rengasamy, 1983; Rengasamy et al., 1984). Oster et al. (1980) have suggested that the high dispersivity of illite was due to "bad" contact between the terraced planar surfaces of illite and its edges. Our results also showed that each of homoionic illite clay had the lowest comparative ζ-potential at equivalent conditions to kaolinite and montmorillonite. These results lend further weight to the requirement of incorporating clay mineral suite within predictive models, which will require some quantitative measure of mineralogy, or a probabilistic modelling approach.

4.5.5. Dispersed suspension versus aggregated system

Both ionicity and the net negative charge have clear effects on the dynamics of clay particle dispersion. However, it must be noted that this work investigated clay suspensions in various solutions and the dynamics of flocculation conditions. It has been clearly established in soil structural science that clay flocculation is not equivalent to soil aggregation (Dang et al., 2018c; Quirk, 2001). We used suspensions to infer relative differences in fundamental particle dynamics as driven by solute conditions. These mechanisms will be valid within aggregated systems, but the predictive model derived in this work is not suitable for application in an aggregated system. Therefore, the outcomes of this work now need to be investigated for aggregated systems with particular reference to reduction in hydraulic conductivity as a proximal measure for clay swelling (inter and intra crystalline swelling) prior to dispersion, and the aggregate-dispersion boundary. Using this work in such an approach will be important to the prediction of soil-specific dispersive thresholds.

4.6. Conclusion

This study investigated the effect of changing pH on dispersive behaviour of Mg and K homoionic clays of three contrasting clay mineralogy, in comparison to Ca and Na clays under equivalent pH conditions, in relation to the ionicity concept. The effect of Mg on clay dispersion was close but greater than that of Ca, while the effect of K was similar but less than Na, under similar pH reading. The dispersive behaviour of Na, K, Mg and Ca homoionic clays was a function of the ionicity indices of clay-cation bonds, with the degree of clay dispersion explained by the pH, EC, ionicity, ζ-potential and mean particle size of the clay-cation system, but not as a single equation. The pH as a predictive factor was dropped with the introduction of net negative charge in Equation 2. Prediction of dispersion-flocculation conditions using Equation 4.2 was good where dispersion was greater than 12.7% dispersed clay. The predictive model was developed for a clay suspension and should not be expected to apply directly to an aggregated system.

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5. Reduction of hydraulic conductivity and loss of organic carbon in non-dispersive soils of different clay mineralogy is related to magnesium induced disaggregation

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5.1. Abstract

Irrigation water containing appreciable amounts of magnesium (Mg) is increasingly used in farming. However, studies on the effect of Mg on soil permeability and structural stability are limited and the results are contradictory. In this study, four soils of different dominant clay mineralogy, specifically kaolinite, illite and montmorillonite, were used to investigate the effect of Mg on saturated hydraulic conductivity (K_{sat}), interaction with organic carbon and soil clay dispersion and to compare to the effects of Ca. The soils were packed in columns and leached with four groups of either Ca-Ca, Ca-Mg, Mg-Mg or Mg-Ca solutions at the successive concentrations of 0.5, 0.25, 0.1, 0.05, 0.025, 0.01, 0.005, 0.001 and 0.0001 M, and finally with deionised water. K_{sat} was measured and leachates were assessed for dissolved organic carbon (DOC) and dispersion as turbidity. The leached soils were tested for aggregate stability, mechanical dispersion and zeta potential. This study showed that Mg had a disaggregation effect on soil structural stability. As compared to Ca, K_{sat} on Mg treated cores were lower over a wide range of concentrations, desorption of DOC and turbidity from Mg clay surface was higher, although the dispersion in leachates was insignificant under both Mg and Ca treatments. The effect of Mg treatment was more pronounced on smectic and illitic soils. The decrease in K_{sat} was related to Mg induced disaggregation, due to intra-crystalline swelling and/or the inter-crystalline swelling in Mg treated soil clays.

Keywords

Magnesium; calcium; saturated hydraulic conductivity; dissolved organic carbon; turbidity.

5.2. Introduction

Pore shape, size distribution and pore continuity are key factors affecting the function of a soil, which directly influences the movement of water, expressed as permeability. It is well known that the concentration and the composition of the percolating solution has a great influence on the structural stability and the hydraulic conductivity (K) of soil (Ali et al., 2018; Aringhieri and Giachetti, 2001; Dang et al., 2018a; Dang et al., 2018c; Levy and Van Der Watt, 1990; Pupisky and Shainberg, 1979; Quirk and Schofield, 1955). In most soils, the deterioration of structure and hydraulic conductivity occurs when electrolyte concentration decreases (de Menezes et al., 2014; Ezlit et al., 2013; Jayawardane, 1979; McNeal and Coleman, 1966) and/or monovalent ions increase (Bennett et al., 2016b; Jayawardane et al., 2011; Rengasamy and Marchuk, 2011). There are emerging examples that irrigation waters containing appreciable amounts of magnesium (Mg) are used in farming, due to the scarcity of good quality irrigation water (Karimov et al., 2009; Qadir et al., 2018; Skilton et al., 2000; Vyshpolsky et al., 2008). However, to date, there are only a few studies on the effect of Mg on soil structural stability and saturated hydraulic conductivity (K_{sat}), relative to calcium (Ca) and sodium (Na) effects (Curtin et al., 1994b; Dontsova and Norton, 1999; Emerson and Chi, 1977; Keren, 1991; Reading et al., 2012; Rengasamy et al., 1986). The results of these studies suggested Mg itself can decrease soil structural stability, which is the definition of "Mg specific effect" referred to in the literature (Curtin et al., 1994b). However, decrease in structural stability is somewhat ambiguous, as slaking, dispersion and disaggregation (expansion of clay domain without dispersion) all contribute to structural instability. Disaggregation is a state in between absolute stability and dispersion, where soil aggregate does not spontaneously disperse (Bennett et al., 2019). When the ionic strength of the equilibrium solution is decreased, the repulsive pressure increases while the attractive pressure decreases due to the development of diffuse double layers. Consequently, the distance between the clay particles increases. Soil disaggregation can also occur due to the intra-crystalline swelling in the presence of 2:1 smectictic clay.

The specific effect of Mg has been observed for the K_{sat} of illite and "occasionally" montmorillonite soils, but is suggested to rarely affect kaolin soils (Alperovitch et al., 1981; Emerson and Chi, 1977; Keren, 1991; Quirk and Schofield, 1955; Zhang and Norton, 2002). The lower effect on K_{sat} in Kaolinitic soil, than for other soils, may be related to the common existence of sesquioxides in kaolinite soils or soils being acidic (Arias et al., 1995; Frenkel et al., 1978; McNeal and Coleman, 1966; McNeal et al., 1968), although any definitive reasoning is unclear. Rahman and Rowell (1979) reported that Mg had no specific effect on montmorillonite soils, arguing that K_{sat} is simply controlled by exchangeable sodium percentage (ESP) and solution concentration, and clay swelling is the dominant process causing structural deterioration. In contrast, exchangeable Mg (in the presence of Na) has been shown to have a specific effect on K_{sat} of a non-calcareous montmorillonite soil, but not of a calcareous one (Alperovitch et al., 1981). This observation does not refute the work of Rahman and Rowell (1979), but tends to suggest that Mg exacerbates the effect of Na. Later, Keren (1991) reported that Mg had a significant effect on erosion and infiltration rate when montmorillonite soils were exposed to rainfall regardless of $CaCO_3$ content in soils, while Zhang and Norton (2002) reported a specific Mg effect, compared with Ca, on the K_{sat} and clay dispersion of two humid-region soils containing smectite, kaolinite, vermiculite and illite. It is clear that the specific effect of Mg is not well established in terms of its mechanism, its operation, or the scale on which it might act. We suggested that the specific effect of Mg is mainly due to its induced disaggregation. It means that physical/chemical bonds are potentially able to overcome the effect, which could explain the observation with soils containing $CaCO_3$. Surface erosion does not negate this reasoning, as montmorillonitic soils in an unconfined environment, such as the surface where erosion occurs, are prone to instability when subject to kinetic energy and the energy of wetting. Hence, further investigation is required to elucidate the extent and mechanism of Mg specific effect on the K_{sat} of soils with the consideration of their mineralogy.

There is a paucity of literature concerning the interaction between Mg and organic matter in terms of soil structural stability. In soil aggregates, both organic matter and clay contribute to the cation exchange capacity (CEC) of soils, and their interactions have a major influence on soil structural stability (Nelson and Oades, 1998). Organic matter may enhance or prevent soil dispersion depending on its nature. Goldberg et al. (1990) found that adding dissolved organic matter enhances clay dispersion, and claimed that the positive effect of organic matter on soil structure probably occurs through binding of soil particles by roots and hyphae at the aggregate level, but at the clay-particle level the negative charge of organic anions enhances clay dispersion. Other researches indicated that when organic matter content is high in soils, water interaction leading to clay dispersion is minimal because charge on clays is reduced by clay-organic bonds, which are mostly covalent, or soil aggregates are enveloped by organic materials formed by covalent bonding (Marchuk and Rengasamy, 2012; Marchuk et al., 2013a). Marchuk et al. (2013a) observed that NaCl caused higher dissolution of organic carbon than KCl in soils containing smectite and illite-kaolinite, which was in line with the finding that exchangeable sodium led to higher clay dispersion than potassium. However, there is limited literature existing on this same phenomenon for Mg, as far as the authors are reasonably aware. Therefore, investigation into the interaction of Mg with soil organic matter is prudent in driving our understanding of soil structural dynamics.

This study aimed to investigate the impact of exchangeable Mg on the K_{sat} of soils, as compared to Ca treatment at the equivalent condition, whereby soil clay mineralogy was contrasting, *i.e.* montmorillonite, illite and kaolinite. Secondly, the investigation aimed to explore the interaction between permeate Mg and soil organic carbon by measuring the dissolved organic carbon (DOC) from the collected leachate. The hypotheses of this study are that: 1) Mg reduces K_{sat}, as compared to Ca, induced by disaggregation, rather than dispersion; 2) the difference between the K_{sat} of Mg and Ca varies dependent on clay mineralogy and soil texture; and, 3) DOC concentrations from Mg leached samples are greater than those form Ca leached samples, with this related to reduction in K_{sat}, but not dispersion of soil primary particles.

5.3. Materials and methods

5.3.1. Soil used

To control for the effect of pH on soil clay dispersion and hydraulic conductivity, four soils with neutral pH were selected. All four soils were collected from 0–10 cm depth at each site. Soil samples were air-dried, carefully ground and sieved to pass a 2 mm threshold. The physical and chemical properties for the soil samples are presented in Table 5–1. Soil pH and electrical conductivity (EC) were measured in a 1:5 soil/water suspension. The exchangeable cations were determined using method 15A2 as per Rayment and Lyons (2011). The effective cation exchange capacity (CEC_{eff}) was calculated as a sum of exchangeable Na, K, Mg and Ca. Sodium absorption ratio (SAR), cation ratio of soil structure stability (CROSS), exchangeable sodium percentage (ESP) and exchangeable dispersive percentage (EDP) were calculated according to Rengasamy and Marchuk (2011) and Bennett et al. (2016a). Particle size distribution was determined using the method of Gee and Bauder (1986). Water-dispersible clay was measured in the same procedure as particle size analysis without any pre-treatment or chemical addition (FAO, 2014). Clay mineralogy was examined using X-ray diffraction: Soil M4 was classified as a Black Vertosol and was montmorillonite dominant; Soil D6 was classified as a Black Vertosol and was montmorillonite and kaolinite dominant; the Urrbrae soil was a Red Chromosol that was illite dominant, with traces of kaolinite and quartz; while the Timberlea soil was classified as a grey Chromosol and the dominant mineral was kaolinite with traces of illite.

Table 5–1 Selected soil physical and chemical properties and locations

Soil	***units***	***M4***	***D6***	***Urrbrae***	***Timberlea***
Depth	*cm*	0–10	0–10	0–10	0–10
pH		7.3	6.7	6.7	6.3
EC	*dS/m*	0.18	0.19	0.15	0.05
Exchangeable Na	*$cmol_c/kg$*	1.21	0.43	0.12	0.11
Exchangeable K	*$cmol_c/kg$*	0.94	0.42	0.67	0.37
Exchangeable Mg	*$cmol_c/kg$*	16.61	7.26	0.91	1.07
Exchangeable Ca	*$cmol_c/kg$*	26.33	13.17	6.41	2.00
CEC_{eff}	*$cmol_c/kg$*	45.08	21.29	8.10	3.56
ESP	*%*	2.68	1.2	1.44	3.16
EDP	*%*	5.21	2.9	6.46	10.13
Organic carbon	*%*	1.02	1.01	1.50	1.54
Dominant clay mineral [a]		M	M, K	I	K
Taxonomic class[b]		Black Vertosol	Black Vertosol	Red Chromosol	Grey Chromosol
Texture		Clay	Sandy clay	Sandy clay loam	Sandy loam
Clay content	*%*	56	36	29	15
Silt content	*%*	14	8	17	17
Sand content	*%*	30	56	54	68
Water-dispersible clay	*%*	35	20	13	8
Location		Dalby, QLD	Dalby, QLD	Adelaide, SA	Gore, QLD

[a] I, illite; K, kaolinite; M, montmorillonite

[b] Soil classification according to Australian soil classification (Isbell, 1997; 2016)

5.3.2. Hydraulic conductivity

Soil columns were prepared by packing 85 g of sieved soil (air dried, <2 mm) into a plastic cylinder (10 cm length, 4.25 cm diameter). Whatman No. 1 filter papers were placed beneath and above the soil surface of each soil column. To investigate the effect of Mg on K_{sat} as compared to Ca, four groups of solutions, labelled as G1, G2, G3 and G4, were applied. The columns were wetted from the bottom using the baseline solutions, *i.e.* G1 and G2, 0.5 M of $CaCl_2$; G3 and G4, 0.5 M of $MgCl_2$, and kept saturated. The columns were then leached with 25 pore volumes (appro. 1 L) of the treatment solution, *i.e.* 0.5 M $MgCl_2$ or 0.5 M $CaCl_2$ to replace exchangeable Na and K to reach maximum occupation on the exchange sites with Mg or Ca. Subsequently, the soil columns were leached with a series of percolating solutions with decreasing electrolyte concentration: 0.25 to 0.0001 M $CaCl_2$ for G1, 0.25 to 0.0001 M $MgCl_2$ for G2, 0.25 to 0.001 M $MgCl_2$ for G3 and 0.25 to 0.0001 M $CaCl_2$ for G4. As a final solution, deionised water was used to leach each soil. Detailed experimental design is presented in Table 5–2. The solution was applied with a constant hydraulic head of 30 mm for each column.

During leaching, montmorillonite clays underwent initial intra-crystalline swelling, with the change in boundary condition measured, and the head height readjusted. Any deviation from this head height was recorded in order to ensure that hydraulic calculations were sufficiently reflective of the changed conditions. The K_{sat} was recorded and calculated using Darcy's equation. Twelve soil columns were prepared for each group, including three columns for K_{sat} measurement and nine further columns for destructive measurement of exchangeable cations after each leaching solution.

Table 5–2 The ionic composition and concentration of baseline treatment solutions and subsequent leaching solutions used to treat four soils of different clay mineralogy

Group No.	**Baseline treatment**	**Subsequent leaching solutions**								**Final solution**
G1	0.5 M $CaCl_2$	$CaCl_2$ concentrations in leaching solutions (M)								DI water
G4	0.5 M $MgCl_2$	0.25	0.1	0.05	0.025	0.01	0.005	0.001	0.0001	
G2	0.5 M $CaCl_2$	$MgCl_2$ concentrations in leaching solutions (M)								
G3	0.5 M $MgCl_2$	0.25	0.1	0.05	0.025	0.01	0.005	0.001	0.0001	

5.3.3. Leachate characterisation

The leachate of each treatment solution was collected periodically and the turbidity of the leachate was measured using a Hach Turbidimeter 2100N. Then the leachates were filtered through 0.45 µm filter paper and DOC concentration was measured using a TOC–L Shimadzu Total Organic Carbon Analyzer.

5.3.4. Exchangeable cations of treated soils

After completion of each percolating solution for each treatment, the soil was removed from the column, air-dried, crushed, and passed through a 2-mm sieve. The EC of the treated soils was measured at soil water ratio of 1:5. The exchangeable cations were extracted according to the method 15A2 as described in Rayment and Lyons (2011) and measured on ICP-MS.

5.3.5. Critical flocculation concentration of soil clays

Clay suspensions (<2 microns), separated from each soil without chemical treatment (Jackson, 2005), were equilibrated in 1 M $MgCl_2$ or $CaCl_2$ solutions. The excess salts were removed using the dialysis method until EC<0.05 dS/m. 30 mL of clay suspension (1.0 g/L) was pipetted into a 50 mL falcon tube. The initial turbidity of each sample was measured. A series of concentrations of $MgCl_2$ or $CaCl_2$ solutions were then added into Mg or Ca clay suspension respectively. The critical flocculation concentration (CFC) was recorded as the sum of the addition of $MgCl_2$ or $CaCl_2$ at the point the turbidity of clay suspension was less than 5% of the initial turbidity at a depth of 5 cm in 4 h.

5.3.6. Soil dispersion assessment after leaching with DI water

The soils were collected and air-dried after DI water leaching. Aggregate stability test was conducted in order to assess soil aggregate dispersion (Loveday and Pyle, 1973). The soil aggregates were collected from the middle section of soil core, and then carefully immersed into DI water. A visual judgment (scores) was made according to the degree of dispersion. In addition, mechanical dispersion test was performed to examine soil dispersive behaviour under external energy input (Rengasamy, 2002). The turbidity of the colloidal sample was measured. The zeta potential was measured on dispersed clays using a Malvern Zetasizer Nano-ZS analyser.

5.3.7. Statistical analysis

The average value of K_{sat} for each soils at each leaching solution was plotted with standard deviation as error bar. The significant differences between Mg and Ca treatments were investigated using ANOVA single factor test, in terms of DOC values, turbidity and zeta potentials. Statistical significance was established as $\alpha<0.05$. Statistical tests were performed with Minitab software.

5.4. Results and discussion

5.4.1. Exchangeable cation percentage after each treatment

The results of exchangeable cation percentage after each treatment of the four soils are shown in Appendix A.2. The exchangeable calcium percentage (ECP) or exchangeable magnesium percentage (EMP) were greater than 91% after the baseline solution treatment, depending on the cation type of the treatment solution. The ECP values of G1 and the EMP values of G3 remained largely unchanged during following treatments even after leaching with deionised water. For G2 (Ca-Mg), after leaching with 0.25 M $MgCl_2$ solution, the ECP dropped from >91% to <4% while EMP surged >91%. In contrast, for G4 (Mg-Ca), after percolating with 0.25 M $CaCl_2$, EMP decreased to <6%, while ECP increased to >91% and maintained at this level for the remaining leaching at lower concentrations. In general, the amount of exchangeable Na and K was lower than the untreated soils after baseline leaching and throughout the following leaching.

5.4.2. Evaluation of hydraulic conductivity

The K_{sat} of the four soils after each leaching treatment is shown in Fig. 5–1. After baseline treatment (0.5 M), the K_{sat} values of all Mg treated soils were lower than that of Ca treated soils, regardless of clay mineralogy. An initial increase of K_{sat} was observed for all soils when leached with successive solutions of $MgCl_2$ (G3, Mg-Mg) or $CaCl_2$ (G1, Ca-Ca). The greatest K_{sat} of the Mg treated M4 soil column 3.33 cm/hr was found when 0.01 M $MgCl_2$ was used, which was twice the baseline K_{sat} value of 1.64 cm/hr. The greatest K_{sat} for the Ca treated M4 soil was found at 0.005 M $CaCl_2$, which increased by 80% compared to its Ca baseline K_{sat}. The D6 soil, like the M4 soil, was classified as a Vertosol, having the greatest K_{sat} value at 0.005 M in the Mg treatment and 0.001 M in the Ca treatment, increasing by 63% and 27% compared to the equivalent baseline K_{sat} value, respectively. For the Urrbrae soil, the initial increase of K_{sat} ceased after leaching with 0.25 M solutions and was 25% (Mg) and 37% (Ca) greater than baseline values. An initial increase was also found in the Timberlea soil with the greatest K_{sat} reached at 0.05 M, for both the Ca (12% greater) or Mg (25% greater) treatment.

The initial increase of K_{sat} can be related to the decrease of viscosity of $MgCl_2$ and/or $CaCl_2$ leaching solutions. The K_{sat} is inversely proportional to the viscosity of the leaching solution and is proportional to the intrinsic permeability of the porous media (*k*) (Artiola et al., 2004; Jarsjö et al., 1997). According to Haynes (2014), when the concentration of $MgCl_2$ and $CaCl_2$ solutions decreases from 0.5 to 0.025 M, their respective viscosity decreases from 1.22 to 1.02 mPa·s and 1.16 to 1.01 mPa·s. At even lower concentration of $MgCl_2$ and $CaCl_2$, the viscosity of solutions remained largely unchanged and close to that of pure water, *i.e.* 1.00 mPa·s, as shown in Fig. 5–2. Therefore, when the viscosity of percolating solution was decreased by 12% (*e.g.* $MgCl_2$ from 0.5 to 0.05 M), K_{sat} was expected to increase to a similar degree, if the *k* value of soil was stable. The results showed that the K_{sat} values of all soils under either Mg or Ca treatment increased by more than 12%, with the magnitude of K_{sat} increase, and the concentration where the greatest increase occurred, varying with the soil and the cation type used in the leaching solution. It is noted that the viscosity decrease magnitude was less than the K_{sat} increase magnitude, suggesting there is a further mechanism acting. That is, Mg and Ca leaching may improve soil structure, due to greater covalent bonding formed between the divalent cation Mg (or Ca) and clay particles by replacing exchangeable monovalent cations Na and K (Marchuk and Rengasamy, 2011; Marchuk et al., 2013b). There were negligible amounts of exchangeable Na and K left on exchange sites after Mg and Ca treatments. Consequently, the k and K_{sat} values were increased.

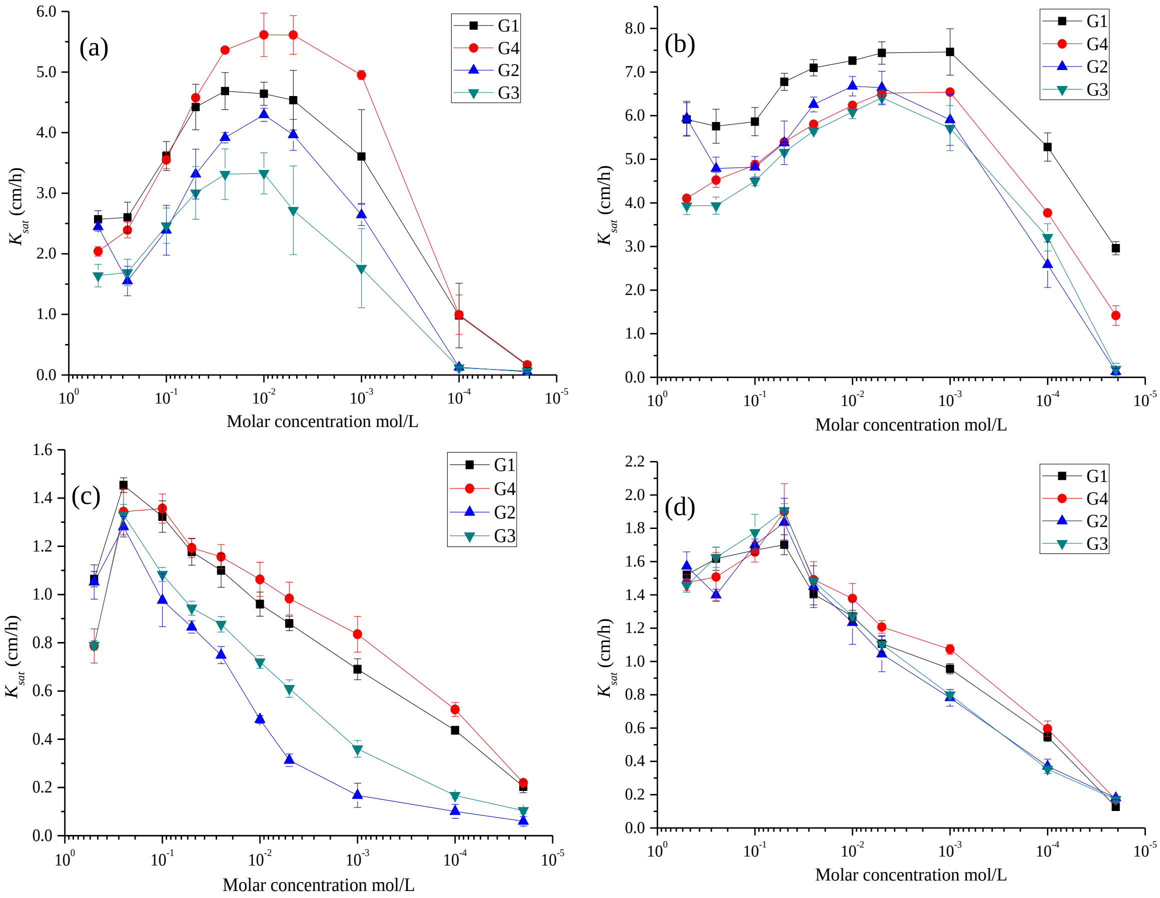


Fig. 5–1 The K_{sat} (cm/h) against molar concentration of percolating solutions (log scale) of four soils leaching with four groups of solutions (a) M4 soil, (b) D6 soil (c) Urrbrae soil (d) Timberlea soil

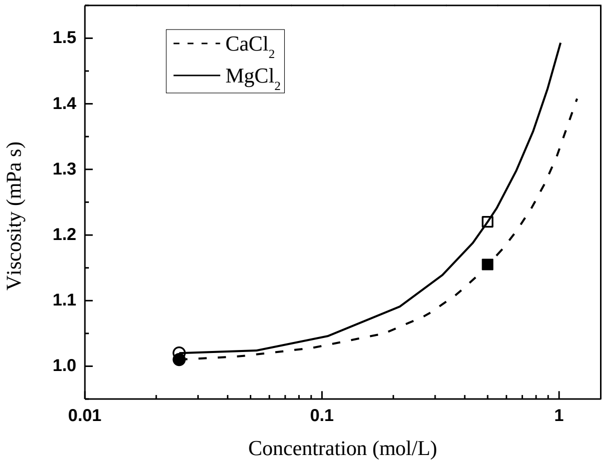


Fig. 5–2 The viscosity (mPa·s) of $MgCl_2$ and $CaCl_2$ solution of different concentrations at 20 °C. □ 0.5M $MgCl_2$; ■ 0.5M $CaCl_2$; ○ 0.05M $MgCl_2$; ● 0.05M $CaCl_2$. The viscosity of pure water at 20 °C is 1.002 mPa·s. Data extracted from (Haynes, 2014).

However, in Urrbrae soil, the K_{sat} started to decrease when the ionic strength of the leaching solutions was <0.25 M. The K_{sat} value of Urrbrae soil was still maintained above or equal to the initial baseline (0.5M), even with 0.025 M solution. A rapid reduction in K_{sat} was observed after leaching with 0.001 M solution, which was in good agreement with the measured CFC of Urrbrae soil (Table 5–3). In addition, rapid reduction of K_{sat} was found in M4 and D6 soils when leached with 0.0001 M solution, and 0.001 M for Timberlea soils, which was in good agreement with the measured CFC for each of the soils.

Table 5–3 The critical flocculation concentration (mmol) of homoionic Mg and Ca soil clays

	M4	D6	Urrbrae	Timberlea
Mg	0.66	1.08	2.73	2.73
Ca	0.57	0.85	1.62	1.89

When DI water was used, the K_{sat} of the M4 soil was reduced to less than 2% of the baseline K_{sat}. Reduction in K_{sat} of the D6 soil was evident in both G1 and G3 treatments after leaching with 1.0 L of DI water. When the electrolyte concentration decreased, divalent montmorillonite crystals had limited crystalline swelling due to the hydration of ions and surfaces of the clay platelets (<1.9 nm), which was supported by Norrish and Quirk (1954). However, the work from Posner and Quirk (1964) showed that for Ca and Mg saturated montmorillonite, the change in basal spacing from 1 to 1.55 nm is not affected by the electrolyte concentration, whereas the transition from 1.5 to 1.9 nm can be regarded as an osmotic effect depending on the charge density and origin in montmorillonite. The osmotic repulsive pressure was much less for divalent cations than monovalent cations, hence divalent montmorillonite particles separated by large distances (>2.5 nm) can collapse together if this force is insufficient to counterbalance the van der Waals attractive forces (Norrish, 1954). Therefore, the volume change of the clay beyond the crystal swelling is attributed to the osmotic phenomenon and is associated with the interactions of the diffuse double layers (Schanz and Tripathy, 2009; Van Olphen, 1977). Unlike montmorillonite, illite and kaolinite are non-expanding clays. Hence, the osmotic swelling due to the ionic concentration gradient between the clay surface and the pore water was the main mechanism in explaining the reduction of K_{sat}. Montmorillonite soils (both M4 and D6 soils) had the greatest reduction in absolute K_{sat} value, compared to the illite and kaolinite soils, which was related to the great affinity to adsorb water (swelling capacity) of montmorillonitic soil clay, due to its expanding nature, larger surface area and CEC than other clay minerals.

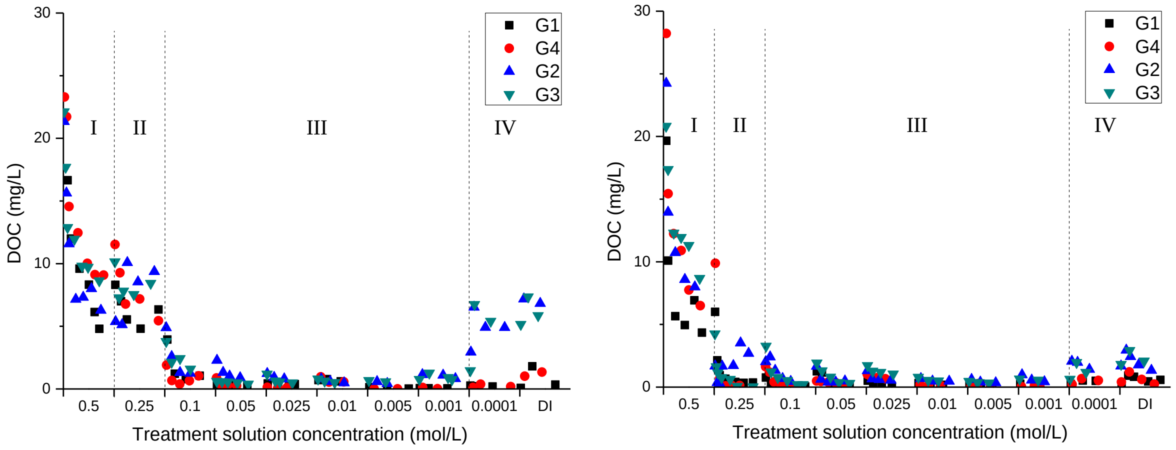
The difference in structure and hydraulic conductivity between the M4 and D6 soils could be related to the clay texture and the abundance of montmorillonite clay. The D6 soil contained 20% less clay and 26% more sand than the M4 soil. Furthermore, the clay minerals in D6 are a mixture of montmorillonite and kaolinite, rather than montmorillonite only in M4. Upon soaking of $CaCl_2$ or $MgCl_2$ baseline solutions, the soil surface rose approximately 13 mm in height for the M4 soil, while this increase was only 4 mm for the D6 soil. This difference in expansion is in general agreement with the relative greater abundance of montmorillonite clay in the M4 soil.

For the other two treating groups (G2 Ca-Mg and G4 Mg-Ca), the K_{sat} values are also plotted in Fig. 5–1. When Ca-saturated soil was leached with 0.25 M $MgCl_2$ solution (G2, Ca-Mg), an evident reduction in K_{sat} was found as compared to that leached with 0.25 M $CaCl_2$ (G1, Ca-Ca). To the contrary, when Mg-treated soils were leached with $CaCl_2$ solution (G4, Mg-Ca), clear increase in K_{sat} was found as compared to that leached with $MgCl_2$ solution (G3, Mg-Mg). During successive leaching, the G4 treatment reached the greatest K_{sat} value at the same concentration as the G1 treatment for each soil, while the G2 treatment reached the greatest K_{sat} at the same concentration as the G3 treatment at equivalent condition. It is important to note the fact both Mg and Ca resulted in an increased K_{sat}, which supports a reversible process. Such reversibility cannot occur for a dispersed soil. However, in most cases, soils leached with Ca solutions had greater K_{sat} than those leached with Mg solutions for each of the four soils, particularly at low EC, which demonstrated the effect of Mg on hydraulic conductivity.

5.4.3. The interaction between cations and dissolved organic carbon

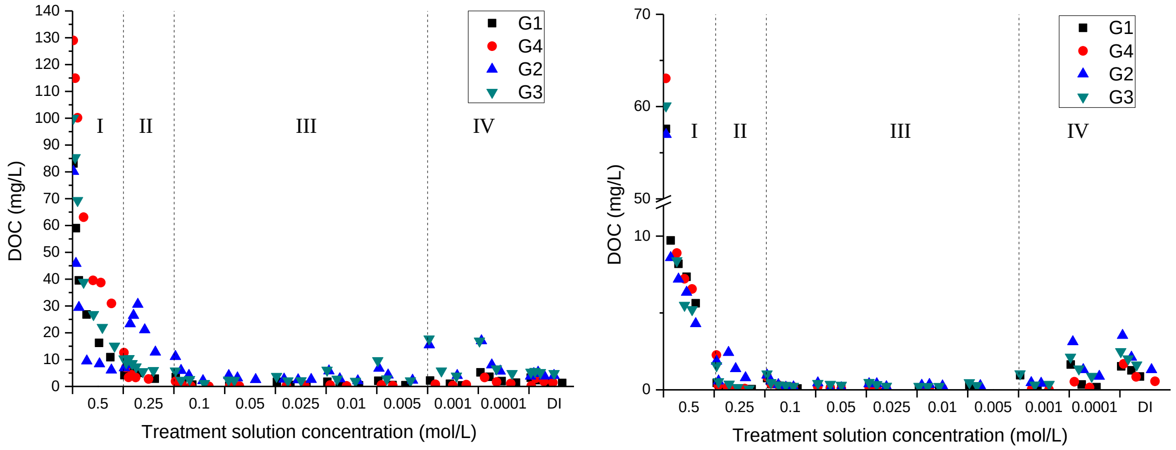
The free movement of DOC is mainly controlled by its adsorption-desorption to soil clay surfaces (Ussiri and Johnson, 2004). In Figure 5–3, four different zones were determined for hydraulic network changes in relation to the changes of DOC from the leachate. In Zone I, initial high DOC values were observed in each soil and then DOC dropped quickly as 1.0 L of baseline solution percolated over, irrespective of the cation dominating the solution. The initially high DOC values in the leachate were due to flushing of soluble organic matter dissolved during wetting, which can be attributed to the response of the faster-cycling carbon pools that contribute most of the decomposition flux (Wong et al., 2010). There was no significant difference ($P<0.05$) in DOC values between Mg and Ca treatment in Zone I for each soil. However, it was evident that during baseline solution leaching, loss of DOC from Mg-treated soils was greater than for Ca-treated soils under equivalent conditions.

In Zone II, a clear increase (>50%) of DOC was observed in each soil with the G2 treatment (Ca in Zone I, changing to Mg in Zone II); *i.e.* 0.25 M $MgCl_2$ solution leached through Ca treated soil samples. The DOC values did not increase immediately upon leaching with $MgCl_2$ solution, but increased beyond the Ca system DOC leaching levels after approximately 150 mL (≈4 pore volumes). This indicated that the increase in DOC was due to replacement of exchangeable Ca with Mg. In contrast, for the G4 treatment (Mg in Zone I, changing to Ca in Zone II), where Mg treated soil was leached with 0.25 M $CaCl_2$, the DOC values decreased significantly. This demonstrates that Mg has a distinct effect on the adsorption-desorption behaviour of organic carbon to clay surfaces.



(a) M4 soil

(b) D6 soil



(c) Urrbrae soil

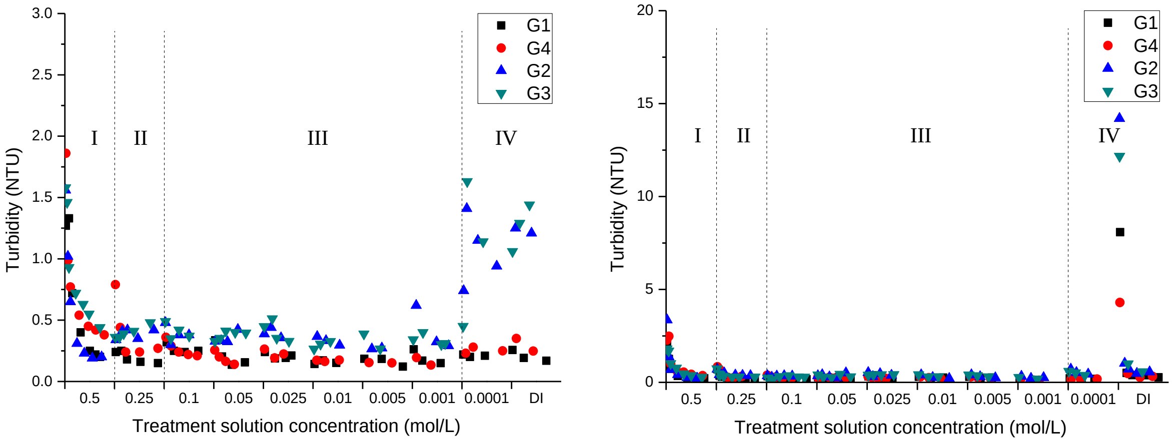
(d) Timberlea soil

Fig. 5–3 The DOC values collected from the leachates for four groups (G1, G2, G3 and G4) of four soils (a) M4 soil (b) D6 soil (c) Urrbrae soil (d) Timberlea soils; (zones I, II, III and IV are explained in the text).

In Zone III, where the concentrations of the leaching solution were below 0.25 M, the DOC values of both Ca treated and Mg treated remained very low. This is mainly because the easily soluble organic matter has been flushed during the previous leaching. Within this range of EC, there was no evident effect on desorption of DOC from clay minerals. Once the leaching concentration was below the CFC (*i.e.*, M4 0.0001 M, D6 0.0001 M, Urrbrae 0.001 M, and Timberlea 0.001 M), where the K_{sat} value of each soil began to reduce significantly, it is noted the DOC values of the Mg treated soils started to increase correspondingly (Zone IV). This can be related to the primary particles in soils leached with low EC solutions separating, allowing clay swelling/disaggregation to occur, which can increase the accessibility and availability of covered SOM and accelerate carbon loss (Oades, 1984). It was noted that DOC of Ca treated soils was 60% less than Mg treated soils in Zone IV. This suggests Mg induced disaggregation results in the removal of carbon from the system through desorption processes

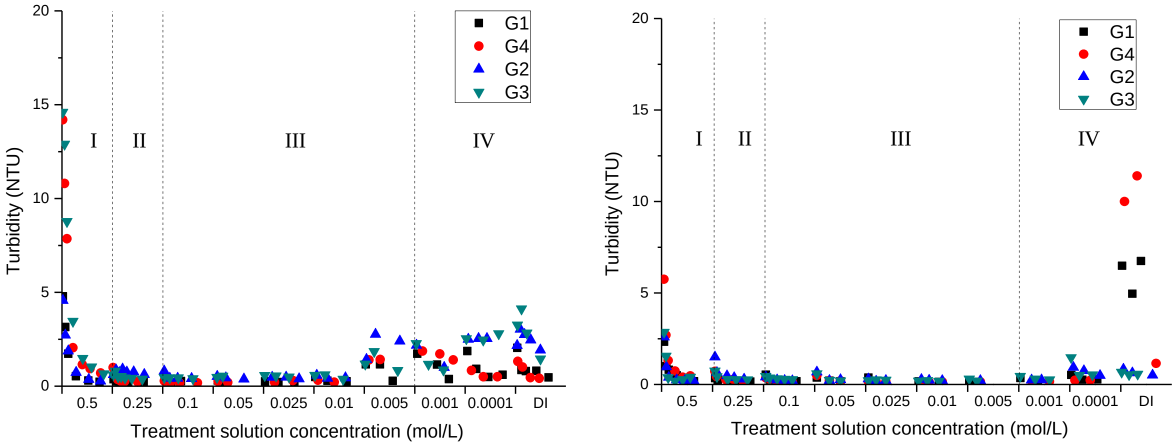
5.4.4. Evaluation of leachate turbidity

As shown in Fig. 5–4, the turbidity of the leachate was maintained at extremely low levels (<20 NTU; 0.016 % dispersed clay from soil) throughout the entire leaching process (Zhu et al., 2016). The same divisional Zones for each soil used in DOC figure were applied here. In Zone I, turbidity values decreased quickly as the baseline solution percolated through. The Urrbrae soil had the highest initial turbidity compared to the other three soils; *i.e* the Mg treated Urrbrae soils had initial turbidity of 15 NTU while Ca treated Urrbrae soils had 5 NTU. In Zone II, there was no significant difference ($P<0.05$) between G2 (Ca-Mg) and G1 (Ca-Ca) treatments, or G4 (Mg-Ca) and G3 (Mg-Mg) treatments, which indicates that the replacement between Ca and Mg was unlikely to have caused dispersion at high EC. In Zone III, the turbidity value remained extremely low, regardless of being Mg-treated or Ca-treated. In Zone IV, a slight increase of turbidity value in each soil was observed when low EC solution was leached. According to Quirk (2001), the solution concentration where dispersed clay particles appeared in the percolate is defined as turbidity concentration, and is usually in the order of 1/8 of the flocculation concentration. When the concentration of percolating solution was several times below the CFC (*i.e.* M4 and D6 soil <0.0001 M, Urrbrae and Timberlea <0.001 M), soil clay dispersion is expected to occur. However, the turbidity values of the leachate subsampled at concentration much less than the CFC (Zone IV), even leached with 1.0 L of DI water, were extremely low (<15 NTU), irrespective of the treatment or soil. This can be partially explained by the fact that the flocculation of a clay suspension is not directly equivalent to a soil aggregation system (Quirk, 2001), whereby in comparison to extracted soil clay, soil aggregates are built up of structural units of various sizes held together by organic matter and other binding agents (Tisdall and Oades, 1982). However, even for an aggregated system we expect to find dispersed clay in the leachate when the aggregation-dispersion boundary is breached (Dang et al., 2018c; Quirk and Schofield, 1955), which could reasonably be expected at the low EC of the experimental DI treatment. The extremely low turbidity of leachate suggested that Mg had negligible effect on causing soil clay dispersion, which was very similar to the effect of Ca.



(a) M4 soil

(b) D6 soil



(c) Urrbrae soil

(d) Timberlea soil

Fig. 5–4 The change of turbidity values of the leachates collected from four groups (G1, G2, G3 and G4) of four soils (a) M4 soil (b) D6 soil (c) Urrbrae soil (d) Timberlea soils; (zones I, II, III and IV are explained in the text).

5.4.5. Soil dispersion assessment after leaching with DI water

To further assess the potential for Mg to cause soil clay dispersion, the aggregate stability test was conducted (Table 5–4). Instant slaking was observed in all soil aggregates upon immersion with DI water, while no dispersion was observed, irrespective of Ca or Mg treatment for any of the soils.

The turbidity and zeta potential measured from mechanical dispersion test are shown in Table 5–4. For the Timberlea soil (kaolinite dominant), minimal difference in turbidity values between Mg and Ca treatments was observed in mechanical dispersion tests. This observation was in line with limited difference in K_{sat} between Mg and Ca treatment, due to the low CEC of kaolinite and low clay content of Timberlea soil. For the other three soils, Mg-treated soil demonstrated greater turbidity than the Ca treatment. In particular, mechanical dispersion of Mg treated M4 soils had 2800 NTU, while Ca treated M4 soil had 2300 NTU at similar condition. Zhang and Norton (2002) found that Mg had a more deleterious effect on high montmorillonite containing soil. However, the zeta potential of each soil clay suspension showed that the two montmorillonite soils (M4 and D6) had lower zeta potential than illite and kaolinite soils. Therefore, it was reasonable to assume that the relatively high turbidity shown in M4 and D6 soils were partially related to their high clay content. It was further noted that the zeta potential of Mg and Ca treated soil were >-30 mV, meaning soil clays were expected to conform to flocculation conditions (Molina, 2013). In addition, the difference of zeta potential between Mg and Ca treatments was minimal (<1.2 mV), *i.e.* no significant difference ($P<0.05$), suggesting Mg behaved similarly to Ca, causing minimal dispersion. In summary, the results from the aggregate stability test and zeta potential support the fact dispersion has not occurred in Mg treated soils without external mechanical force, rather increased disaggregation presumably due to enhanced inter-crystalline swelling and/or the diffuse double layer development inter-crystalline swelling, meaning the clay domains remain non-dispersive.

Table 5–4 The turbidity and zeta potential measured from mechanical dispersion test

Soil	Treated group	Aggregate stability test score	Turbidity NTU	Zeta potential mV
M4	G1	0	2347	-20.8
	G2	0	2896	-21.3
	G3	0	2723	-21.6
	G4	0	2260	-20.9
D6	G1	0	798	-22.4
	G2	0	1120	-23.6
	G3	0	953	-23.5
	G4	0	689	-23.0
Urrbrae	G1	0	1421	-26.5
	G2	0	1685	-27.7
	G3	0	1669	-27.1
	G4	0	1321	-26.8
Timberlea	G1	0	587	-29.5
	G2	0	663	-30.1
	G3	0	634	-29.9
	G4	0	595	-29.1

5.4.6. The disaggregation effect of Mg on soil structural stability

The results of this work allow us to accept the three hypotheses that: 1) Mg reduces K_{sat}, as compared to Ca, induced by disaggregation, rather than dispersion; 2) the difference between the K_{sat} of Mg and Ca varies dependent on clay mineralogy and soil texture; and, 3) DOC concentrations from Mg leached samples are greater than those from Ca leached samples, with this related to reduction in K_{sat}, but not dispersion of soil primary particles.

This study demonstrated that over a wide range of concentrations, Mg had an effect on soil structural stability by reducing K_{sat} as compared to Ca. This was evidenced by:

1) In most cases, greater K_{sat} values for soil leached with $CaCl_2$ solutions (G1; Ca-Ca) than for those leached with $MgCl_2$ solutions at equivalent conditions (G3; Mg-Mg), irrespective of soil clay mineralogy;

2) An abrupt reduction in K_{sat} was observed when Ca treated soils were leached with $MgCl_2$ solutions (G2; Ca-Mg), as compared to G1 (Ca-Ca) for all of the four soils; and,

3) An obvious increase in K_{sat} found for Mg treated soils subsequently leached with Ca (G4; Mg-Ca), as compared to a maintained Mg equivalent condition (G3; Mg-Mg).

According to Rengasamy et al. (1986), when the percolating solution exceeded the flocculation values, hydraulic conductivity was not affected by either SAR or Ca/Mg ratio. However, the results in this study showed that Mg had a reducing effect on $K_{sat,}$ and thereby soil structural stability, even when the concentration of the percolating solution was well above the CFC. This can be related to Mg induced disaggregation, due to the occurrence of lattice intra-crystalline swelling in montmorillonite clays and/or diffuse double layer development, inter-crystalline swelling when electrolyte concentration decreases (Bennett et al., 2019). Furthermore, the disaggregation effect of Mg is also related to its degree of covalent bonding between clay and Mg cations. Despite both Ca and Mg having similar charge, the two cations have different ionic potential (Huheey et al., 1993) and Misono’s softness parameter (Sposito, 2008). Consequently, as compared to Ca, the Mg treated soils had a lower degree of covalency in clay-cation bonding (Marchuk and Rengasamy, 2011), which caused smaller mean particle size (aggregation size), lower porosity and lower hydraulic conductivity (Marchuk et al., 2013b), on this basis. The greater turbidity values of Mg treated soils in the mechanical dispersion test, than for those of Ca treated soil, occurred with minimal difference in zeta potential, which can also be partially attributed to the small mean particle size of Mg soil clays. Thus, Mg clay suspension would have required more time to achieve full flocculation (Stokes law). This is a very important result, as it changes the way that we expect Mg to interact within the soil system; *i.e.* Mg is not directly responsible for dispersion, but could be expected to exacerbate the effects of monovalent ions on soil dispersion.

The results also demonstrated that Mg had a disaggregation effect on soil structural stability through increasing desorption of DOC from clay surfaces, as compared to Ca, whereby replacing Ca with Mg solution, even at high EC, resulted in more DOC being removed from the soil system. Furthermore, leachate from the Mg treatments always contained more DOC than the Ca treated soils. These suggested that the loss of organic carbon is related to Mg induced disaggregation, which can increase the accessibility and availability of covered SOM and accelerate carbon loss. Moreover, Ca improves soil structure stability through cationic bridging with clay particles and soil organic matter, as it can effectively link clays with permanent negative charges to anionic functional groups on organic matter (Bronick and Lal, 2005; Churchman et al., 1993; Oades, 1984; Singh et al., 2016). From this study, Mg has shown a greater capacity than Ca for desorption of DOC, which suggests Mg is less effective than Ca in forming strong bonds between negatively charged clay minerals and DOC through cation bridging. The Mg bond is less covalent and more ionic in nature than Ca (Marchuk and Rengasamy, 2011), meaning water molecules can break the covalent Mg bonds easier than that of Ca.

The results also indicated that the degree of disaggregation effect of Mg on K_{sat} and DOC varied depending on clay mineralogy and texture. The difference in K_{sat} between Mg and Ca baseline treatments was as large as 35% in the two Vertosols, while it was 25% for the Urrbrae soil (illititic) and 4% for Timberlea soil (kaolinitic). Similar results were reported by Zhang and Norton (2002) that the K_{sat} of a smectitic soil leached with 0.01 M Mg solution was 35% less than that leached with 0.01 M Ca solution, while on the other hand, 13% difference was reported for an illite dominant soil. The low initial K_{sat} values and high turbidity values in mechanical dispersion tests of Mg montmorillonite soils, as compared to Ca montmorillonite soils, were partly due to the difference in covalency degree between Mg and Ca ions, and partly due to the high CEC of montmorillonite clay and high clay content. To the contrary, there was less difference between Mg and Ca on the K_{sat}, DOC and mechanical dispersion of the Timberlea soil, as compared to the other three soils. This is mostly likely because of the low clay percentage in the Timberlea soil, as well as kaolin being the dominant clay. With lower surface area and CEC, the exchangeable cations had less impact on kaolin than illite and montmorillonite clays. In this work, three contrasting mineralogies were selected in order to explore the effect of clay mineralogy on the obtained results. However, future work should seek to consider this aspect of the work in order to incorporate such relationships into predictive models.

5.5. Conclusions

This study demonstrated that Mg had a disaggregation effect, rather than dispersion effect, on soil structural stability when compared to the equivalent condition of Ca by reducing K_{sat} and increasing desorption of DOC from the clay surface. An initial increase of K_{sat} was observed for each soil when leached with a successive of $MgCl_2$ solutions (electrolyte concentration above 0.005 M), with the extent and point of occurrence of the highest K_{sat} depending on the dominant soil clay mineralogy and the type of cation in the leaching solution. When electrolyte concentrations of leaching solution were below CFC, rapid reduction in K_{sat} was detected in all four soils, but to a different extent. The low turbidity of leachates in all soils suggested that Mg clay domains are non-dispersive. However, mechanical dispersion testing demonstrated that the presence of Mg on the exchange sites results in higher dispersion than Ca caused under additional force or intensive cultivation operations.

The results of this study demonstrated that Mg has deleterious effect on soil structural stability compared to Ca, due to disaggregation processes, and determines with confidence that Mg is not the direct cause of dispersion. The degree of the disaggregation effect of Mg on saturated hydraulic conductivity and the release of the dissolved organic carbon largely depends on the electrolyte concentration of the soil solution and dominant clay mineralogy.

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6. Re-examining the flocculating power of sodium, potassium, magnesium and calcium for a broad range of soils

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6.1. Abstract

Cation ratio of soil structural stability (CROSS) and exchangeable dispersive percentage (EDP) have been recently proposed to replace the traditional sodium absorption ratio (SAR) and exchangeable sodium percentage (ESP) for predicting soil structural stability, in conjunction with the electrolyte concentration. Both CROSS and EDP incorporate the dispersive effects as coefficients transforming K and Mg effects to equivalent Na and Mg (dispersive) or Ca (flocculative) effects. However, these coefficients are derived from the flocculating power of Na, K, Mg and Ca based on a limited number of soil clays. This study re-examines the flocculating power for a broad range of soil clays by analysing their critical flocculation concentrations (CFCs). Soil clays from 17 contrasting soils were separated and chemically treated into Na, K, Mg and Ca homoionic clays. Within the same cation treatment, there were significant differences among the measured CFC values, which can be related to their different clay mineralogy and co-existing materials in soil clays. The dispersive coefficients of K and Mg, as well as the flocculative coefficient of Mg, were seen to vary substantially in respect to the generalised values used in CROSS and EDP. The absolute errors between the specified CROSS and generalised CROSS as well as the specified EDP and generalised EDP have been calculated for the 95th percentile of possible cation concentrations. In terms of CROSS, the dispersive coefficient *a*[K] and flocculative coefficient *b*[Mg] both contribute to the absolute error, with *a*[K] having a greater influence than *b*[Mg]. In terms of EDP, the dispersive coefficient *a*[K] played the dominant role in causing absolute error between the specified EDP and generalised EDP, while the role of dispersive coefficient *c*[Mg] was not significant. The outcome of this work indicates that the soil-specific coefficients should be used to minimise

the possibility of undue soil structural degradation, while the generalised coefficients are only applicable to a small range of outcomes.

Keywords: Flocculating power, Cation ratio of soil structural stability (CROSS), exchangeable dispersive percentage (EDP), sodium adsorption ratio (SAR), exchangeable sodium percentage (ESP), dispersion

6.2. Introduction

Degradation of the soil hydraulic network, due to clay dispersion, is a major concern producing adverse impacts on agricultural productivity and sustainability. Conventionally, exchangeable sodium (Na) – interacting with other factors including electrolyte concentration, pH and clay mineralogy – has been considered to be the major mechanism controlling soil clay dispersion (Rengasamy and Olsson, 1991; Sumner et al., 1998). However, exchangeable potassium (K) and magnesium (Mg) have more recently been demonstrated to contribute to soil aggregate dispersive and disaggregation behaviour (Bennett et al., 2016a; Dang et al., 2018a; Rengasamy and Marchuk, 2011). K systems have been demonstrated as dispersive in the presence of minimal Na, with varying effects at the same K concentration for different soils (Dang et al., 2018b), while there is evidence to suggest that Mg systems are dispersive (Curtin et al., 1994b).

Traditional definitions and thresholds for soil dispersion are reliant on Na, via the exchangeable sodium percentage (ESP), or the sodium adsorption ratio (SAR). ESP is defined to be the exchangeable Na content normalised by the cation exchange capacity (CEC), multiplied by 100 to obtain a percentage:

$$ESP = \frac{[Na^+]}{CEC} \times 100\% \qquad \text{Eq. 6.1}$$

Here both Na and CEC are conventionally measured in cmol$_c$/kg, and CEC is usually considered to be the sum of exchangeable [Na], [K], [Mg] and [Ca], but can be measured directly. SAR is an indicator of the potential soil structural hazard of monovalent [Na] within a solution, as offset by the divalent [Ca] and [Mg], accounting for the divalent charge:

$$SAR = \frac{[Na^{+}]}{\sqrt{\frac{[Mg^{2+}] + [Ca^{2+}]}{2}}} \qquad \text{Eq. 6.2}$$

Here the cation concentrations are in mmol_c/L and the SAR is an index for the potential sodium exchange when the solution interacts with charged clay surfaces. The SAR also attributes an equivalent flocculating effect to each of Mg and Ca. Australian efforts to characterise sodic soil suggest that it disperses in a situation when ESP>5 (McIntyre, 1979), or ESP≥6 (Northcote and Skene, 1972), or at SAR≥3 (Rengasamy and Olsson, 1991). These two traditional indices do not consider the potential negative effects of K and Mg, and this limitation justifies a basis for new indices that can adequately account for these differential effects.

To obtain a more comprehensive soil dispersion prediction, a number of researchers have attempted to quantify the effect of K and Mg on soil structural stability, in comparison with Na and Ca, and then modified the predictive equations by adjusting the coefficients of K and Mg. For example, the study of Levy and Van Der Watt (1990) showed that an increasing amount of exchangeable K in the soil clay results in a decrease in the hydraulic conductivity, and that its specific effect lies between the Na and Ca. Smiles and Smith (2004) suggested the monovalent cation adsorption ratio (MCAR), used to predict soil structural stability, which included K in the calculation of SAR by assuming both the K and Na to have equal effects. However, the study of Levy and Van Der Watt (1990) has already demonstrated this perspective to not always model real soils. The differential effects of K, in comparison with Na, is further supported by numerous authors (Bennett et al., 2016a; Dang et al., 2018b; Marchuk et al., 2013a; Rengasamy and Marchuk, 2011).

In terms of Mg, Emerson and Chi (1977) suggested that Mg had a specific effect on the dispersion of illite, also deducing that Mg was about one-tenth as effective as an equivalent amount of exchangeable Na in causing the dispersion. However, the study of Curtin et al. (1994b) suggested that the exchangeable Mg was less effective, and in fact, only about 4% to 5% as effective as exchangeable Na. This supports the calculations of Bennett et al. (2016a), who suggested it to be 3.7% as effective as Na. Emerson and Bakker (1973) worked with red-brown earth subsoils, containing illite as the dominant clay mineral (65-80%), and found that only about 3% of the exchange sites were occupied by Na ions when Mg was the complementary cation in order to disperse the soil. When Ca was the complementary cation, about twice as many Na ions were required. This cumulative body of literature clearly demonstrates the differential behaviour of K and Mg with respect to both Na and Ca, indicating the need to revisit the original formulations through a detailed sensitivity analysis.

To develop a means to account for the differential effects of K and Mg, Rengasamy and Sumner (1998) used the critical flocculation concentration (CFC) values for K-, Mg-, and Ca-saturated clays, extracted from four kinds of soils, which they used to calculate the average relative flocculating concentration of each cation:

$$r\mathrm{CFC}_{\mathrm{X}} = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{X_{CFC}}{\mathrm{Ca}_{CFC}}\right)_i \qquad \text{Eq. 6.3}$$

Here, *i* denotes the i^{th} sample of soil for the *n* samples, while the subscript CFC denotes that values are critical flocculation concentrations of the cation (*X* and Ca*).* The average relative concentration required was found to be within the ratio of 45:27:1.8:1 for Na:K:Mg:Ca (Rengasamy and Sumner, 1998). Consequently, if the flocculating power of Na equals to 1, the flocculating power of the cations would be K=1.8, Mg=27, and Ca=45 respectively. Using Na as the basis instead of Ca allows the dispersive equivalence of a cation X to Na, i.e. X_{disp}, to be calculated:

$$\mathrm{X}_{disp} = \frac{\mathrm{Na}_{FP}}{X_{FP}} \qquad \text{Eq. 6.4}$$

where X_{FP} denotes the flocculating power of the cation X. Furthermore, the flocculating equivalence of Mg as compared to Ca is:

$$\mathrm{Mg}_{floc} = \frac{\mathrm{Ca}_{FP}}{\mathrm{Mg}_{FP}} \qquad \text{Eq. 6.5}$$

Using the flocculation power, compared to Na, K was calculated to be 0.556 (=1/1.8, from Eq. 6.4) as effective in causing the dispersion. In contrast, Mg is 0.037 (1/27, using Eq. 6.4) as effective as Na in causing dispersion and 0.60 (27/45, using Eq. 6.5) as effective in aiding flocculation as Ca.

These coefficients have been further applied in the concept of exchangeable dispersive percentage (EDP, Eq. 6.6; Bennett et al., 2016) and the cation ratio of soil structural stability (CROSS, Eq. 6.7; Rengasamy and Marchuk 2011). EDP and CROSS account for the different behaviours of K and Mg, and replace ESP and SAR, respectively. Modifying Eq. 6.1 to incorporate these coefficients yields:

$$EDP = \frac{[Na^{+}] + 0.556[K^{+}] + 0.037[Mg^{2+}]}{CEC} \times 100 \qquad \text{Eq. 6.6}$$

where the K and Mg coefficients calculate an equivalent dispersive effect to Na and all concentrations are in the units of $cmol_c/kg$. Bennett et al. (2016a) also explained that the Mg term in Eq. 6.6 should only be used where sufficient Mg exists in the system, which is a function of the Ca:Mg cations ratio and the concentration of the cations other than Ca and Mg. Where Mg is insufficient, the inclusion of the Mg term can potentially impact adversely on the prediction of clay dispersion (Bennett et al., 2016a).

Modifying Eq. 6.2 with the flocculating power to include the dispersive equivalence of K to Na, and flocculating equivalence of Mg to Ca, leads to:

$$CROSS = \frac{[Na^{+}] + 0.556[K^{+}]}{\sqrt{\frac{0.6[Mg^{2+}] + [Ca^{2+}]}{2}}} \qquad \text{Eq. 6.7}$$

where all concentrations are in the units of $mmol_c/L$ and the dispersive effect for Mg is not included directly, but as a difference in the flocculation compared to Ca.

Noting that the coefficients for K and Mg in Eq. 6.6 and 6.7 are the arithmetic mean of the four soils, a number of recent studies, including Smith et al. (2015), Bennett et al. (2016a) and Dang et al. (2018b), have shown that these coefficients are optimisable and variable. This suggests that they are indeed affected by a number of factors, and they also could be considered as soil-specific. Furthermore, Smith et al. (2015) proposed a more general definition of $CROSS_{opt}$ through the optimization of the two coefficients using irrigation water composition, and this study demonstrated a better correlation with the threshold electrolyte concentration (C_{TH}), rather than the CFC:

$$CROSS_{opt} = \frac{[Na^{+}] + a[K^{+}]}{\sqrt{\frac{b[Mg^{2+}] + [Ca^{2+}]}{2}}} \qquad \text{Eq. 6.8}$$

Here a and b are the optimizable coefficients of dispersive equivalence of K and flocculative equivalence of Mg respectively. Smith et al. (2015) defined a and b by the threshold electrolyte concentration, measured as a 15% reduction in saturated hydraulic conductivity, rather than the CFC, as was the basis of CROSS (Rengasamy and Marchuk, 2011). It is important to note, at this point, that Quirk and Schofield (1955) did not define the occurrence of C_{TH} due to dispersion, but rather the process of both inter- (swelling due to diffuse double layer development termed disaggregation) and intra-crystalline swelling (2:1 clay mineral swelling) (Bennett et al., 2019; Dang et al., 2018d). Indeed, (Quirk, 2001) redescribes the turbidity threshold (C_{TU}) many years later to highlight that it occurs at approximately one quarter of the solution concentration as the C_{TH} for a given SAR and is the point that describes the initial occurrence of dispersion. On the other hand, the C_{TH} describes bulk property behaviour of clay domains, where in reality clay domains are likely to differ in size, meaning it is possible that negligible dispersion occurs concurrently for smaller clay domains, carrying less surface charge, to swelling and disaggregation process that dominate the C_{TH} phenomenon (Bennett et al., 2019; Dang et al., 2018c; Ezlit et al., 2013; Quirk, 2001). Therefore, the use of C_{TH} as a threshold for dispersion might not be completely warranted. On this basis, Bennett et al. (2016a) maintained the use of CFC in their suggestion of a generalised equation for EDP based on exchangeable cations:

$$EDP_{opt} = \frac{[Na^{+}] + a[K^{+}] + c[Mg^{2+}]}{CEC} \times 100 \qquad \text{Eq. 6.9}$$

Here a and c are the optimizable coefficients of dispersive equivalence of K and Mg respectively, and a can be considered the same as in Eq. 6.8. It is noteworthy that the c[Mg] term is only used where the magnesium effect is 40%, or above, that of a pure Mg system, which is a function of other cation concentrations (Bennett et al., 2016a).

In terms of Eqs.6.8 and 6.9, the physical effects on CROSS and EDP caused by variation of the coefficients is unclear. Bennett et al. (2016a) had demonstrated that the inclusion of the Mg term resulted in both improvement and a worsening of soil stability prediction, depending on Mg concentration being above or below the 40% threshold (discussed above), respectively. Furthermore, literature has suggested that Mg does have a dispersive effect (Rengasamy et al., 1986). In re-visiting the CFC, there is value in investigating the extent of coefficient variation, and its effect, as well as the likelihood of contribution to dispersion from Mg. Considering these important issues, the purpose of this research is to investigate the extent the apparent soil-specificity of the coefficients of K and Mg, as compared to Na and Ca, affects the soil stability metrics. To fulfil these objectives, a range of soils with a varying level of pH and clay mineralogy are selected to re-examine the coefficients (*i.e.*, quantify the individual and cumulative effects of Mg and K) through a critical flocculation concentration study in line with that undertaken by Rengasamy and Sumner (1998).

6.3. Material and method

6.3.1. Soils used

Seventeen soils with different clay mineralogy, clay content, pH and EC were used in this study. Soil samples were air-dried and gently ground to pass a 2 mm sieve. The physical and chemical properties of the soils are given in Table 6–1. Soil pH and electrical conductivity (EC) were measured in 1:5 (gram of soil/cm^3 volume of solution) ratio, using the method 4A1 and 3A1 from Rayment and Lyons (2011). The exchangeable cations were extracted using method 15A2 from Rayment and Lyons (2011), and analysed using a PerkinElmer inductively coupled plasma–mass spectrometer (ICP–MS). The effective cation exchange capacity (CEC_{eff}) was calculated as the sum of exchangeable Na, K, Mg and Ca. The values of SAR, and ESP were calculated using Equation 2 and Equation 1, respectively. CROSS and EDP were calculated using Equation 7 according to Rengasamy and Marchuk (2011) and using Equation 6, as per Bennett et al. (2016a). Soil texture was determined as per Gee and Bauder (1986). Clay mineralogy was examined by X-ray diffraction method on an ARL 9900 workstation, using Co Kα radiation operated at 40 kV and 40 mA. The organic carbon was measured using the method from Walkley and Black (1934).

Table 6–1 Properties of soil samples

Soil	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
pH	9.2	9.1	8.5	8.2	7.4	7.3	7.3	6.9	6.7	7.4	8.9	8.7	8.7	6.6	4.5	5.3	5.2
EC (dS/cm)	0.37	0.15	0.18	0.63	0.09	0.15	0.19	0.18	0.14	0.05	0.34	0.12	0.3	0.05	0.08	0.05	0.02
Clay (%)	49	42	54	46	26	56	62	36	29	13	29	36	34	15	15	10	10
Silt (%)	41	42	38	6	12	14	16	8	17	5	13	60	16	17	23	10	5
Sand (%)	10	16	8	48	62	30	22	56	54	82	58	4	50	68	62	80	85
Soil texture[a]	SiC	SiC	C	SC	SCL	C	C	SC	SCL	LS	SCL	SiCL	SCL	SL	SL	SL	LS
Organic carbon (%)	0.4	0.3	0.5	0.6	1.6	1.0	1.3	1.0	0.7	1.6	1.1	0.6	1.6	1.5	1.5	1.6	1.3
CEC (cmol$_c$/kg)	29.3	19.7	47.1	17.1	22.9	45.1	39.4	21.3	8.1	3.6	13.9	12	11.3	3.6	1.8	1.2	1.2
EDP (%)	13.9	3.1	3.3	11.0	2.0	5.2	12.4	4.4	6.5	2.3	4.4	3.6	12.5	10.1	5.2	10.0	9.5
CROSS (mmol$_c$ L^{-1})$^{0.5}$	7.8	2.1	1.9	6.7	0.3	2.0	3.5	1.1	0.6	0.5	2.5	1.0	4.6	1.2	1.2	2.5	2.0
ESP (%)	11.4	1.6	1.5	9.9	0.4	2.7	9.5	2.0	1.4	0.5	3.0	0.3	11.7	3.2	3.2	7.7	7.5
SAR (mmol$_c$ L^{-1})$^{0.5}$	5.3	0.9	1.0	6.0	0.2	1.9	3.1	1.0	0.3	0.1	1.9	0.1	4.3	0.8	0.9	1.9	1.8
Dominant clay mineral[b]	M	M	M	M	M	M	M	M	I	K	K	K	K	K	K	K	K

[a] SiC, silty clay; SCL, sandy clay loam; SiCL, silty clay loam; C, clay; SC, sandy clay; SL, sandy loam; LS, loamy sand

[b] I, illite; K, kaolinite; M, montmorillonite

6.3.2. Homoionic clay preparation

The clay suspensions were separated from soils following the approach of Zhu et al. (2016). Forty grams of each soil (<2 mm) mixed with 200 mL of deionised water were shaken overnight. The mixture was then transferred to a 1.0 L cylinder, and filled to the 1.0 L mark with deionised water. After sitting for 24 h, the top 800 mL of the clay suspension was collected — from the <40 cm depth taking care to minimise the pipette suction removing solution for the >40 cm depth, which, according to the Stokes law, contained only clay-sized particles — and passed through a 53 μm sieve to remove the visible organic matter from the colloidal suspension.

The turbidity of the colloidal suspension was measured and the amount of clay was calculated according to Zhu et al. (2016). One gram of clay was then equilibrated with 1M NaCl, KCl, $MgCl_2$ or $CaCl_2$ solutions and shaken overnight. The equilibrium process was repeated twice in order to obtain a mixture as completely homoionic as reasonably possible. Excess electrolytes were removed using the dialysis method until the EC of each homoionic clay was below 0.05 dS/m.

The prepared clays were found to be 91-97% homoionic, determined by measurement on an inductively coupled plasma – mass spectrometer. In the process of removing soluble salts, some hydrolysis occurs (3-5%) in which the exchangeable ions were replaced by polyvalent cations (Mg^{2+}, Al^{3+}) released from the clay crystal (Oster et al., 1980).

6.3.3. The measurement of critical flocculation concentration

The critical coagulation concentrations were determined by the modified method described in Rengasamy and Oades (1977). A 30 mL aliquot of homoionic clay suspension from a concentration of 1g:1000 mL clay:water was pipetted into a 50 mL falcon tube for each soil and homoionic treatment. The initial turbidity of each clay suspension was measured using a Hach Tubidimeter 2100N. A series of different concentrations of NaCl, KCl, $MgCl_2$ and $CaCl_2$ solutions were then added into a corresponding Na, K, Mg or Ca clay suspension. The clay suspensions were agitated three times and left to settle for 4 h. This time period was chosen to allow the sedimentation of the particles >2 μm out of the 5 cm solution depth. The CFC was recorded as the sum of the concentration of electrolytes required to give a clear solution, *i.e.* at the point the turbidity of clay suspension was less than 5% of the initial turbidity. The experiment was undertaken in two replicates for every soil and homoionic solution combination.

6.3.4. Statistical analysis

The critical flocculation concentration values of homoionic soil clays were obtained to (re-)examine the minimum, maximum, mean and unbiased standard deviation. Significant differences between the CFC values for the 17 soil clays within each homoionic cation treatment were determined by an ANOVA single factor analysis with a 95% confidence interval (α=0.05).

It stands that practitioners may still seek to utilise the generalised coefficients for CROSS and EDP on the basis they do not require measurement of the specific CFC. Therefore, a sensitivity analysis was undertaken. This consisted of the error (variation) between CROSS, or EDP, with general coefficients, compared to the respective stability metric with its specific coefficients. The absolute error was utilised so that the units remained the same for both CROSS and EDP, providing a practical physical interpretation:

$$\varepsilon = \left|X_{Spc} - X_{Gen}\right| \qquad \text{Eq. 6.10}$$

Here 'ε' is the absolute error, 'X' is the stability metric of interest, either CROSS or EDP, and the subscript '*Gen*' indicates the use of the generalised coefficients, while the subscript '*Spc*' indicates the specific coefficients were used.

To achieve this, MATLAB R2017b was used to construct a four-dimensional array for the four cation species (*i.e.* [Na], [K], [Mg] and [Ca]), with each dimension representing the variation of a particular species. To compute CROSS, each species' cation concentration was independently varied in the range 0–60 mmol$_c$/L, so that each possible combination of species concentration was used. The upper limit of the concentration was selected as it was the threshold salinity for moderately tolerant crops (Ayers and Westcot, 1985). Similarly for EDP, the species' contribution to CEC was varied in the range 0–100%, with only those species combinations which produced a CEC of 100 considered. This process for EDP ensures that only unique combinations of species concentrations are considered (*e.g.* [Na] = 50 cmol$_c$/kg with no other species produces the same EDP as [Na] = 100 cmol$_c$/kg with no other species, so only the latter is included in the analysis). Approximately 170 000 different combinations of species concentrations were included for fidelity of the statistical analysis.

The specific CROSS was computed for a range of physically-realistic values of a[K] and b[Mg] and compared to the generalised CROSS (a = 0.556 and b = 0.600) using Eq. 6.10. The specific EDP was similarly computed for ranges of a[K] and c[Mg] and compared to the generalised

EDP (a = 0.556 and c = 0.037). The ranges of a, b and c were chosen based on values observed in the current work. To assess the sensitivity of CROSS and EDP to a, b and c, the value of ε at the 95th percentile and the fraction of combinations with $\varepsilon < 1.5$ (%, EDP; $\mathrm{mmol_c}^{0.5}\ \mathrm{L}^{-0.5}$, CROSS) were computed. The 95th percentile provides a robust measure of the largest ε by discounting outliers. The value of 1.5 was chosen on the assumption that the traditional thresholds of SAR and ESP are physically important (it may be that they are not, but that is outside the current scope). Rengasamy et al. (1984) reported that the critical SAR for dispersion is 3, and this value is lower than the ESP critical values for dispersion of 5 (McIntyre, 1979) or 6 (Northcote and Skene, 1972). Therefore, because ε is an absolute error, a 1.5 lower limit was used to acknowledge this value would be both positive and negative.

An underlying assumption in the analysis is that each concentration is equally likely to occur, and that no concentration exceeds 60 $\mathrm{mmol_c}$/L. With the limited data available, it is impossible to obtain a true joint-probability density function for the combinations of cation concentrations, so the numerical results can only be indicative of the range of values of ε. This is still sufficient for the purposes of the analysis.

6.4. Results and Discussion

6.4.1. Determination of the critical flocculation concentration

The CFC values for the homoionic soil clays are shown in Table 6–2. In every sample, the CFC was found to be [Na]>[K]>[Mg]>[Ca]. This sequence was aligned with the degree of ionicity of clay-cation bonds, where Na has the greatest degree of ionicity and Ca has the greatest degree of covalency of clay-cation bond (Marchuk and Rengasamy, 2011). Consequently, Ca clays have the greatest tendency to flocculate, thereby requiring less electrolyte than the other three cations.

Within the same cation treatment, the CFC values varied significantly among the 17 soils (P<0.001). In particular, the CFC values for Na homoionic soil clays were found to be in the range of 5.66–98.11 $\mathrm{mmol_c}$/L with a standard deviation up to 26.86 $\mathrm{mmol_c}$/L. The results demonstrated that the CFC value – the minimum concentration required to flocculate soil clays – for homoionic systems is soil-specific. In general, Na, K, Mg and Ca-saturated montmorillonite dominant soil clays (samples 1–8) appeared to require lower electrolyte concentration to achieve full flocculation than illite dominant clay (sample 9). This result, which agrees with the findings from previous studies (Arora and Coleman, 1979; Oster et al., 1980; Shainberg and Letey, 1984; Zhang and Norton, 2002), is possibly related to the structural difference between the expanding and non-expanding clays. For example, when montmorillonite is dominated by adsorbed Na ions, because of the high swelling between the platelets, a single platelet tends to persist in a more dilute solution (Van Olphen, 1977). However, when the electrolyte concentration is increased in the clay suspension, clay particles generally stick together and begin to form flocs that are likely to settle down (Goldberg et al., 2011). It is noteworthy that the several-fold higher CFC of Na-illite compared to that of Na-montmorillonite is probably due to the smaller edge-to-face attraction force in the Na-illite. This is true because upon a close approach of the clay particles, the mismatch of the terraced illite surface generally leads to a poor contact between the edges and the surfaces, resulting in a smaller edge-to-face force of attraction and, consequently, a higher CFC value for the Na-illite (Oster et al., 1980). For K, Mg and Ca systems, on the other hand, the correspondingly higher CFC value of illite as compared to the montmorillonite systems is likely associated with this edge-to-face attraction force mechanism, although the bivalent montmorillonite could exists in tactoids consisting of several clay platelets whereas a single platelet occurs in a monovalent system (Norrish and Quirk, 1954).

As illustrated in Table 6–2, there are large differences in the CFC values determined between kaolinite dominant clays (samples 10–17). The present findings are consistent with earlier works, for example, those of Arora and Coleman (1979) and Goldberg et al. (2011). In particular, the study of Arora and Coleman (1979) found that the CFC values of the two Na saturated kaolinite clays were approximately 8 and 245 mmol_c/L, respectively. This is probably due to some other materials that exist in the system, such as organic matters, soluble silicates or sesquioxides (Arora and Coleman, 1979; Goldberg and Glaubig, 1987). In general, the majority of the kaolinite clays (samples 10–17) have a greater CFC value compared to those of montmorillonite clays (samples 1–8) in each of the homoionic systems.

Table 6–2 The critical flocculation concentrations (mmol$_c$/L) of homoionic soil clays; *p*-values indicated significant variation between CFC values for the 17 soils within each homoionic treatment of Na, K, Mg or Ca. Significance was tested at a 95% confidence interval.

Soil clay	**Na**	**K**	**Mg**	**Ca**	**Clay**
1	11.28	9.09	0.49	0.36	M
2	5.66	2.60	0.48	0.23	M
3	21.28	7.65	0.96	0.71	M
4	12.46	9.50	0.75	0.55	M
5	15.61	9.50	1.26	0.73	M
6	18.00	9.90	0.66	0.57	M
7	20.00	11.98	1.01	0.74	M
8	18.88	11.61	1.08	0.85	M
9	93.04	42.54	2.73	1.62	I
10	42.63	29.63	2.09	1.05	K
11	14.11	8.25	0.84	0.52	K
12	7.32	5.67	0.49	0.36	K
13	22.84	16.12	1.21	0.85	K
14	98.11	30.32	2.73	1.89	K
15	25.05	18.62	1.68	1.07	K
16	33.61	20.22	1.76	1.25	K
17	22.65	15.83	1.76	1.16	K
Maximum	98.11	42.54	2.73	1.89	
Minimum	5.66	2.60	0.48	0.23	
Mean	28.38	15.24	1.29	0.85	
Standard deviation	26.86	10.4	0.73	0.45	
P value	<0.001	<0.001	<0.001	<0.001	

6.4.2. Relative flocculating powers and calculated coefficients

The relative flocculating concentration (calculated from Eq. 6.3), the dispersive coefficients of *a*[K] and *c*[Mg] (calculated from Eq. 6.4) and the flocculative coefficients of *b*[Mg] (calculated from Eq. 6.5), are listed in Table 6–3. The mean flocculative coefficient of *b*[Mg] of the seventeen soil clays is 0.677, which might be considered close to 0.60 reported in the study of Rengasamy and Sumner (1998), but results in a noticeable skewing in Figure 1. However, the coefficient *b*[Mg] is seen to vary distinctively among the different soils, from about 0.488 to 0.855. On the other hand, the average dispersive effect of *c*[Mg] in this study is found to be 0.055, which is slightly higher than the value of 0.037 reported in the study of Bennett et al. (2016a). This finding agrees with those of Zhu et al. (2019) stating that solution turbidity less than 15 NTU – effectively zero dispersion – was found when highly magnesic soil was leached with deionised water. The results from the present study further suggest that if the effect of Mg on soil clay dispersion is considered as a combined flocculative and dispersive effect, the specific influence of Mg in decreasing the structural stability is overwhelmingly due to disaggregation processes (swelling processes without dispersion; see: Bennett et al. 2019). This is due to decreased covalency in the Mg system, resulting in lower flocculative-ability compared to that of Ca, rather than the highly-limited potential dispersive effect of Mg. In this study, we found that the coefficient *a*[K] occupied a value in the range of 0.309 and 0.777 (with an average value of 0.605), which was relatively close to the value of 0.556 reported earlier (Rengasamy and Marchuk, 2011; Rengasamy and Sumner, 1998). However, the extent of the coefficient range suggests that direct measurement, or an optimisation approach, could be of immense value for inclusion of the influence of K and Mg in structural metrics.

Table 6–3 The relative flocculating powers, dispersive effects of Mg and K and the flocculative effect of Mg

Soil clay	**Na**	**K**	**Mg**	**Ca**	**The dispersive effect of K: *a***	**The flocculative effect of Mg: *b***	**The dispersive effect of Mg: *c***
1	31.94	24.81	1.35	1.00	0.777	0.743	0.042
2	24.35	11.28	2.05	1.00	0.463	0.488	0.084
3	30.08	10.81	1.36	1.00	0.359	0.733	0.045
4	22.55	17.20	1.37	1.00	0.763	0.732	0.061
5	21.32	12.98	1.72	1.00	0.609	0.582	0.081
6	31.81	17.49	1.17	1.00	0.550	0.855	0.037
7	27.11	16.24	1.37	1.00	0.599	0.728	0.051
8	22.11	13.60	1.26	1.00	0.615	0.793	0.057
9	57.58	26.33	1.69	1.00	0.457	0.592	0.029
10	40.53	28.18	1.99	1.00	0.695	0.503	0.049
11	27.17	15.88	1.62	1.00	0.584	0.617	0.060
12	20.11	15.10	1.35	1.00	0.751	0.743	0.067
13	26.71	18.85	1.42	1.00	0.706	0.706	0.053
14	52.02	16.08	1.45	1.00	0.309	0.691	0.028
15	23.35	17.36	1.57	1.00	0.743	0.639	0.067
16	26.89	16.18	1.41	1.00	0.602	0.709	0.052
17	19.49	13.63	1.52	1.00	0.699	0.659	0.078
Maximum	57.58	28.18	2.05	1.00	0.777	0.855	0.084
Minimum	19.49	10.81	1.17	1.00	0.309	0.488	0.028
Mean	29.71	17.18	1.51	1.00	0.605	0.677	0.055
Standard deviation	10.83	4.96	0.24	–	0.140	0.097	0.017

6.4.3. Sensitivity analysis

The sensitivity analysis of CROSS is shown in Fig. 6–1. Within the considered range of cation concentrations, the absolute maximum error between CROSS$_{spc}$ and CROSS$_{gen}$, caused by varying the coefficients *a*[K] and *b*[Mg], was as much as 5.5 mmol$_c^{0.5}$ L$^{-0.5}$, which would cause significant prediction difference for soil structural stability. Based on the suggested critical equivalent threshold of SAR=3 (Rengasamy et al., 1984), and the fact that Bennett et al. (2019) stated that SAR standard error ≈±5.5 was sufficient to suggest that the threshold electrolyte concentration was highly soil-specific, this reinforces that the use of specific coefficients is desirable. As expected, when the coefficients *a*[K] and *b*[Mg] were close to the generalised values 0.556 and 0.600 respectively, the absolute error between CROSS$_{spc}$ and CROSS$_{gen}$ was the smallest. In contrast, when the coefficients *a*[K] and *b*[Mg] increasingly deviated from the generalised values, the absolute error at the 95th percentile increased accordingly. It was noted that the coefficient *a*[K] could potentially have a wider range of values (although not observed in this data set), and that the possible values of *b*[Mg] are skewed to having values much larger than the general value, which is due to the higher average value of *b*[Mg] measured in this study. The percentage of compositions (cation concentrations) with CROSS error ≤1.5 is shown in Fig. 6–1b, indicating that there is a narrow range of *a*[K] and *b*[Mg] combinations that do not result in unacceptable error, however with a ±0.1 change in either coefficient, the probability of unacceptable error quickly approaches 20%, with further small increases exponentially increasing this probability. Overall, the analysis indicates that greater care is required in the value of *a*[K] since it has more potential variability than *b*[Mg], but each should be measured within an accuracy of ±0.1.

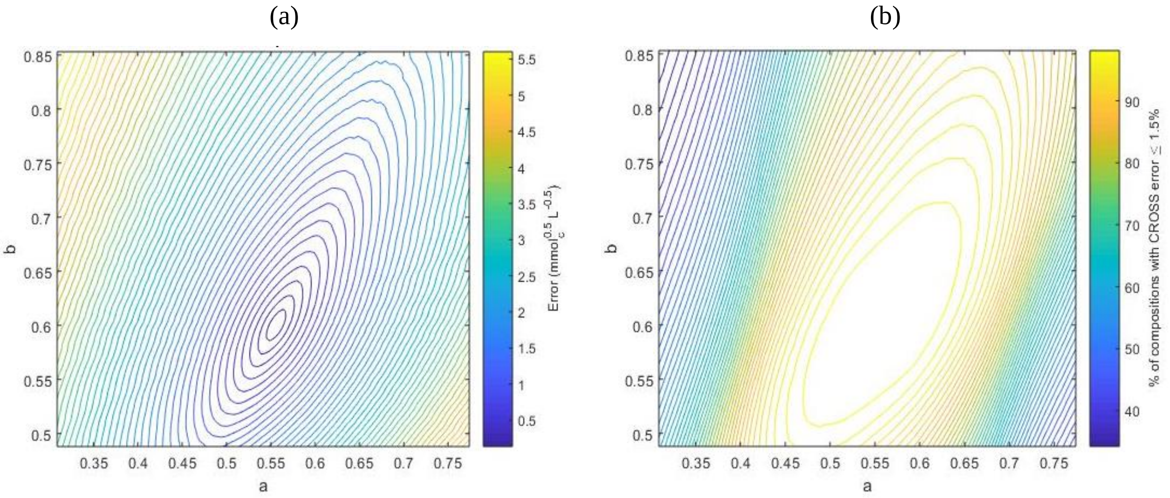

Fig. 6–1 Sensitivity analysis between the specific CROSS and the generalised CROSS as a function of varying coefficients *a*[K] and *b*[Mg], with the consideration of each cation concentration in the range of 0–60 $mmol_c$/L. (a) The absolute error ($mmol_c^{0.5}$ $L^{-0.5}$) at the 95th percentile; and (b) the fraction of compositions with CROSS error ≤ 1.5 $mmol_c^{0.5}$ $L^{-0.5}$.

Figure 6–2 shows the sensitivity analysis for the absolute error between specified EDP and generalised EDP. Within the possible range of the cation concentration – Σ([Na], [K], [Mg],[Ca])=100, assuming no Al or Fe influence – the absolute maximum error between EDP_{spc} and EDP_{gen} caused by varying the coefficients *a*[K] and *b*[Mg] was up to 14%. The coefficient *a*[K] exhibited a dominant influence in determining the absolute error because it is typically an order of magnitude larger than *c*[Mg]. This suggests firstly that, as for CROSS, it is important to determine the specific coefficient for K, and secondly that it is not necessary to use *c*[Mg] when computing EDP because the error in EDP caused by not including *c*[Mg] is overwhelmed by the error in EDP caused by measurement errors in a[K]. This latter result was suspected by Bennett et al. (2016a) and can now be confirmed. The percentage of compositions (cation concentrations) with EDP error ≤5% is shown in Fig. 6–2b, demonstrating a narrow range of acceptable values of a[K] (over the range 0.525<0.556<0.595), with any further deviations rapidly increasing the probability of unacceptable error. Therefore, EDP is highly sensitive to small changes in the K equivalence coefficient, and the specific EDP is advised.

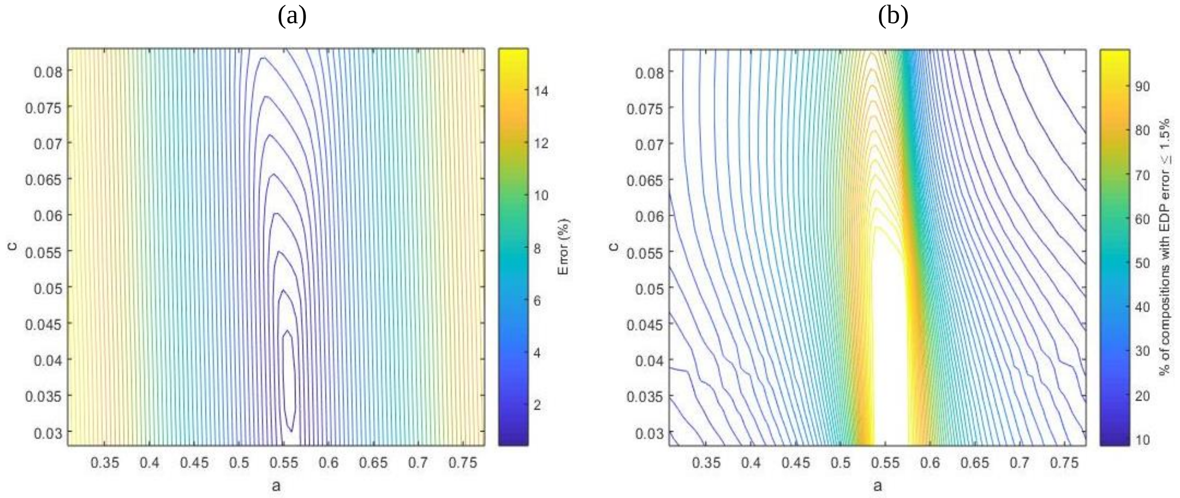

Fig. 6–2 Sensitivity analysis between the specific EDP and the generalised EDP as a function of varying coefficients a[K] and c[Mg], assuming that soil cation exchange capacity equals 100 cmol$_c$/kg. (a) The absolute error (%) at the 95th percentile; and (b) the fraction of compositions with absolute EDP error ≤ 1.5%.

The results from this study confirm that reasonable variation of the coefficients within CROSS$_{spc}$ and EDP$_{spc}$ has the probability of resulting in significant error; with the exception of coefficient c, which can be removed from the EDP equation. On this basis, caution is required when using the generalised values of CROSS and EDP in terms of soil structural stability predictions. Further investigations attempting to incorporate K and Mg effects into dynamic soil structural models will need to consider the specific coefficients for the soils in question, as well as understand how these factors may affect the specificity of these coefficients within the individual soil, but potentially also with time (Dang et al., 2018b). Finally, the results in this work support the removal of the c[Mg] term from the EDP equation, meaning that EDP should be redefined as Equation 6.11:

$$EDP = \frac{[Na^{+}] + a[K^{+}]}{CEC} \times 100 \qquad \text{Eq. 6.11}$$

where the K coefficient calculates an equivalent dispersive effect to Na.

6.5. Conclusions

This study has shown that the CFC values of soil clays can vary significantly, even within the same homoionic cation environment. The variation of CFC is dependent on the soil clay mineralogy and on the other materials present in the soil. The CFC values of the studied homoionic clays were found to follow a sequence of Na>K>Mg>Ca for each of the soil clays, which yielded results that generally comply with the degrees of ionicity of the clay-cation bonds. The coefficients *a*[K], *b*[Mg] and *c*[K] derived from this research study, which were obtained from a greater variety of soils than previous studies, showed substantial differences in the generalised values of 0.556, 0.600 and 0.037, respectively.

Through a numerical sensitivity analysis, variations in both the coefficients *a*[K] and *b*[Mg] were found to significantly affect the absolute error between CROSS_{spc} and CROSS_{gen}. In terms of EDP, the dispersive coefficient *a*[K] had the primary role in determining the difference between EDP_{spc} and EDP_{gen}, while the dispersive coefficient *c*[Mg] had negligible impact and can be removed from the EDP equation, redefining the equation in the same manner that Bennett et al. (2016a) had speculated was appropriate.

The results of this work suggest that obtaining the CFC for a given soil will be important for improving the accuracy of soil structural metrics in the majority of cases, and that some caution is required in the use of the generalised CROSS and EDP equations. Further investigation using the specific CROSS and EDP is required to validate their impacts on the prediction of soil structural stability.

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7. General discussion, conclusion and future research directions

7.1. General discussion

In this thesis, the effect of Mg on soil structural stability has been investigated in both soil clay suspensions and aggregated systems. The outcomes have indicated that Mg results in a disaggregation processes, with the potential for negligible dispersion (turbidity<15 NTU), rather than dispersive processes associated with Na. The major role of Mg is maintenance of soil structural stability, though it is less efficient in aiding flocculation, as compared to Ca. This research has demonstrated that the effect of Mg on structural stability is soil-specific. This chapter provides general discussion on the effect of Mg on soil structural stability and saturated hydraulic conductivity (K_{sat}), together with other influencing factors including clay mineralogy, pH, electrolyte concentration, solution viscosity, texture and organic matter. Controlling mechanisms are also discussed. This chapter further presents the key conclusions of this thesis and recommendations for future works.

7.1.1. Redefining the role of magnesium in soil structural stability

7.1.1.1. The flocculative role vs. the dispersive role of magnesium

The effect of Mg on soil structural stability was investigated based on the work of Rengasamy and Sumner (1998), Rengasamy and Marchuk (2011) and Bennett et al. (2016a). We arbitrarily separated the Mg effect into 1) Mg causing dispersion as equivalent to the effect of Na in a dispersive role, which was denoted with coefficient *c* used in the optimised EDP index, and 2) Mg aiding flocculation in a flocculative role as compared to Ca, which was denoted with flocculative coefficient *b* used in the optimised CROSS index. Through the critical flocculation concentration study of Na, K, Mg and Ca homoionic clays of 17 contrasting soils, the average flocculative coefficient of Mg, as compared to Ca as the baseline is 0.677, with maximum 0.855 and minimum 0.488. The dispersive coefficient of Mg, as compared to Na as the baseline, is in range of 0.028 to 0.084, with an average value of 0.055. On the basis of this, the leaching of artificially-magnesic soils with deionised water, and the conduct of spontaneous and mechanical dispersion tests for artificially-magnesic soils, it can be determined that the dominant role of Mg on soil structural stability is a flocculative role, as Mg itself causes negligible dispersion. Specifically, this conclusion can also be evidenced by:

1) No dispersion observed when contrasting soils were leached with a wide range of $MgCl_2$ solution from 0.5 to 0.0001 M;

2) When magnesic soil was leached with DI water, no visual dispersion was found in the leachate;

3) Through conducting Emerson test, no spontaneous dispersion was exhibited for Mg soil aggregates; and,

4) The zeta potential was >-30 mV in both the Mg homoionic clay and the Mg soil aggregate systems.

Based on the differential flocculating capability of Mg and Ca, and the observed results in this work, it is apparent that the likely contribution to dispersion by Mg is the exacerbation of inter-crystalline swelling, with potential for soils to disperse at lower concentrations of monovalent cations. This supports the findings of Astaraei and Chauhan (1992) and He et al. (2013).

7.1.1.2. Magnesium and Calcium effects on soil structural stability are related to inherent difference in the degree of ionicity of the clay–cation bonds

The different effects between Ca and Mg ions on soil structural stability originates from their inherent differences. Despite the same valence, the ionic radius of Mg is smaller than that of Ca (not to be confused with Mg having a larger hydrated radius than Ca), consequently, ionic potential is greater for Mg than for Ca (Huheey et al., 1993). Therefore, Mg will exert a greater effect in polarizing anions than Ca. However, Mg has a much smaller Misono's softness parameter than Ca, which indicates Mg has less polarizability than Ca (Sposito, 2008). Overall, the covalency degree between the clay and Mg bond was weaker than the bond between the clay and Ca (Marchuk and Rengasamy, 2011). As the tendency to form covalent bonds increases, the proclivity to break the clay-cation bonds in water decreases. Hence, the tendency for Mg clays to reduce hydraulic conductivity (pore geometry) should be greater than that of Ca clays. However, while other effects such as the EC caused by the percolating solution (irrigation and rainfall), mineral dissolution, and montmorillonite hydrolysis having an impact on the soil pore geometry have all been included in the description of the Mg effect on soil structure, the degree of covalency has largely been missing from such descriptions.

In this thesis, ionicity indices, along with soil pH, EC, net negative charge (zeta potential), and particle size, have all been considered to explain the relationship for dispersed clay (%) in a clay suspension. The degree of ionicity of a clay-cation system influences the cation hydration reactions and therefore is expected to correspond to the stability of the soil system (Marchuk and Rengasamy, 2011). With the incorporation of net negative charge, soil pH can be ignored, as the change in net negative charge is a result of change in pH described by Chorom and

Rengasamy (1995). The dominant mechanism of EC effect on clay particle dispersion is via osmotic potential (Quirk, 2001), rather than the effect of EC on net negative charge (Dang, 2018). Using the model described above to predict dispersed clay provided an R^2=79%. These results from a colloidal system clearly support the hypothesis that the disaggregation of an aggregated system is greatly affected by the ionicity. However, the inherent stability of a soil system will be a function of a mixed ion system, meaning that the net ionicity of the system will be dynamic with the change in solution concentration and cation suite equilibrium conditions. With lower degree of ionic bonding, the role of Mg in the presence of monovalent cations is liable to shift towards enhancing dispersion, by decreasing the concentration of monovalent ions required to induce dispersion. This requires further investigation through the lens of the ionicity approach, to move towards a functional model of soil dynamic structural condition.

7.1.1.3. Effect of magnesium on clay dispersion depending on clay mineral, pH, texture and mechanical force

Based on the results from this thesis, Mg itself causes negligible dispersion in the aggregated system without external force, irrespective of clay mineralogy. The Emerson test on Mg saturated soil aggregates showed no spontaneous dispersion, irrespective of montmorillonite, illite or kaolinite soils. Through leaching Mg solutions (0.5 to 0.0001 M) on soil columns, the leachate showed extremely low turbidity values, irrespective of clay minerals. These soil cores were further leached with deionised water, and none of the samples showed dispersion (<15 NTU). Only a slight difference in Mg montmorillonite, kaolinite and illite clays was shown in their net negative charge (ζ-potential) at soil neutral pH. These results appear to suggest that clay mineralogy is not critical in determining the effective action of Mg on soil structural stability in an artificially-magnesic soil, when there is no external disturbance or varying pH.

It is well known that distinctive differences in clay particle size, width to thickness ratio, charge density and origin, and structure exists between montmorillonite, kaolinite and illite clays (Bergaya et al., 2006b; Churchman et al., 1993; Oades and Waters, 1991). The effects of these differences were enhanced, in terms of the behaviour of Mg soil clays, when additional mechanical force and/or changing pH was applied to the system, based on the findings from this thesis. In the study of homoionic clays with changing pH, to extract and prepare the homoionic soil clays, an intensive shaking process was applied. In addition, to measure the dispersed clay, Mg clays were subject to external force, either inverting 3 times (spontaneous dispersion) or 20 times (mechanical dispersion). Consequently, the measured dispersed clay from the clay suspensions cannot be directly applied to soil aggregate system, but the results were useful to facilitate mechanistic investigation. When the mechanical dispersion test was conducted (with external force) in the soil aggregate system, the dispersed clay of Mg saturated soils varied depending on clay minerals and soil texture. Heavy clay textured Mg montmorillonite soil showed the highest dispersion, as compared to kaolinite and illite soils. The Mg montmorillonite soil had the highest zeta potential (highest tendency to flocculate), compared to illite and kaolinite soils, suggesting the high turbidity values under mechanical force were also related to its high clay content. In addition, Mg saturated kaolinite soil had the lowest turbidity, and highest zeta potential, among the studied soils, due to its low clay content and kaolinite as the dominant clay.

It is worthy to mention that, under mechanical force, clay dispersion existed in Mg soils, particularly at neutral pH. However, as indicated by their desirable ζ-potential (>-30 mV), Mg soil clays were all prone to flocculation, irrespective of the mechanical energy. Therefore, while dispersion was observed, it was simply a matter of time in achieving full flocculation (settlement; Appendix A.3), though the discrete time needed was dependent on clay minerals and texture. Nevertheless, the mechanically dispersed clay could form a crusted layer when a surface dries out, although it is extremely important to note that this would have occurred for the Ca system under mechanical energies applied also; it might be that the Ca crust eventuates as more permeable than a Mg one, given the results in this thesis and discussion in above sections, but this is speculation and would require further testing. Crusting of either Mg or Ca systems could cause several problems for plant emergency and crop yields. Therefore, further attention should be provided to mechanical energy and resultant dispersion of magnesic systems, where energy is equivalent to rapid-hydration (absence of kinetic energy), rain droplet impact (rapid-hydration with kinetic energy), cultivation, tramping by animals and other interventions causing stress on soils.

7.1.1.4. Effect of magnesium on saturated hydraulic conductivity of soils depending on electrolyte concentration, solution composition and viscosity, clay minerals and soil texture

In this thesis, four soils, with neutral pH and contrasting dominant clay mineralogy, were leached with a range of Mg solutions (from 0.5 M to 0.0001 M, and eventually DI). An increase of K_{sat} was observed when the percolating concentration of Mg solution was >0.01 M for heavy clay montmorillonite soil, >0.005 M for light clay montmorillonite soil, >0.25 M for illite soil, and >0.05 M for kaolinite soil. The initial increase of K_{sat} was partially due to the decrease of viscosity of $MgCl_2$ (Artiola et al., 2004; Jarsjö et al., 1997). Mg may improve soil structure due to higher covalency bonding between cations and clay particles by replacing monovalent cations. However, to prove this, a real-time monitoring on the pore size at nano and micro sizes during leaching is critical. Furthermore, it is important to note that decreasing electrolyte concentration of leaching solutions may not always leads to the reduction of K_{sat}, which also depends on the solution viscosity and ionic compositions in leaching solutions. Subsequently, it must be noted that both Mg and Ca resulted in an increased K_{sat}, which supports a reversible process. To further explore the mechanism of reversibility, it is also of great interest to use real-time monitoring on the change of pore size of varying clay minerals. A computer tomography approach may be feasible to help determine these pore geometry dynamics without destructive intervention.

The rapid reduction in K_{sat} observed after leaching with 0.0001 M solution for montmorillonite soils and 0.001 M for illite and kaolinite soils was in good agreement with the measured CFC for each of the soil clays. When DI water was used, the K_{sat} values of the four soils were further decreased. From this study, the effect of Mg on K_{sat} of soils has been found to be dependent on electrolyte concentration of the leaching solution, clay minerals and soil texture, which is in direct support of the work of Quirk and Schofield (1955) and McNeal et al. (1968). However, the ability to predict this reduction remains elusive, and premature as compared to threshold electrolyte concentration analysis of Na-Ca systems. Furthermore, Dang et al. (2018b) demonstrated that the apparent coefficient of equivalence to Na-effect for K changed throughout the threshold electrolyte concentration analysis procedure. Similar investigations for Mg based on soil-specific CFC are required to incorporate such structural dynamics for Mg into even semi-empirical models of soil structure.

7.1.1.5. The interaction between magnesium and dissolved organic carbon

In the soil clay system, where particles are <2 µm, organic material is likely to be sorbed onto the clay surfaces and held firmly by the various bonds, which may increase or decrease the attraction between the particles depending on the nature of organic matter (Tisdall and Oades, 1982) and the scale of operation (Bennett et al., 2019). In general, DOC enhances clay dispersion in soils dominant with monovalent ions (Goldberg et al., 1990; Marchuk et al., 2013a). Na causes increased solubility of organic matter as compared to Ca by up to several orders of magnitude (Churchman et al., 1993; Nelson et al., 1996). This thesis demonstrated that Mg increases desorption of DOC from the clay surface, irrespective of clay mineralogy, to a consistently greater level than for a Ca system. On the other hand, given this trend, the DOC from continuous leaching with Ca produced a reasonably similar magnitude to that of the Mg system. This observation suggested the majority of organic matter remained in magnesic soils. In return, when organic matter was high in soils, water interaction leading to clay dispersion was minimal. This can support that minimal dispersion was found in either magnesic or calcic soils. In contrast, as observed through increased DOC, lower amounts of organic matter remained in sodic soil (Nelson et al., 1996; Wong et al., 2010). This may further exaggerate higher dispersion, potentially to a greater level in the presence of Mg, than naturally calcic or magnesic soils. Further investigation of this phenomenon and separation of it from continuous leaching is required.

7.1.1.6. Magnesium induced soil structural deterioration is due to disaggregation: Redefining the specific-effect

The role of Mg in soil dispersion has been a somewhat controversial scientific discussion since the 1960s (McNeal et al., 1968; Van der Merwe and Burger, 1969). Curtin et al. (1994b) defined the individual effect of Mg in decreasing hydraulic conductivity and structural stability as the specific-effect of Mg. This term has been widely used in the studies of Mg effect on soil structural stability (Basak et al., 2015; Dontsova and Norton, 1999; Yousaf et al., 1987b; Zhang and Norton, 2002). However, the actual definition of this specific effect remains vague throughout the literature, and usually refers to exchangeable Mg reducing the hydraulic conductivity of a soil system, with some literature explicitly identifying a dispersive effect, while other literature does not. Curtin et al. (1994b) postulate that the specific-effect of Mg is dominant, based on the evidence that the Mg effect on clay dispersion and reduction in hydraulic conductivity was greater than for a slightly elevated Na concentration within a Mg dominant system. That is, the deterioration of the Mg system outweighed the subsequent deterioration effect of Na addition to the system. In calcareous soils the additional presence of Mg is documented as enhancing the solubility of $CaCO_3$, resulting in greater EC and thus a more stable system, while in non-calcareous soils the additional Mg results in lower hydraulic conductivity (Alperovitch et al., 1981; Alperovitch et al., 1985). Additionally, Shainberg et al. (1988) suggests that Mg affects the hydrolysis of montmorillonites, resulting in a lower EC, and explains the reduction in these soils as a function of reduced osmotic pressure. Rengasamy and Sumner (1998) build on the potential mechanisms further by exploring the CFC, and subsequently introducing the ionicity and covalency effects of Mg, whereby the ionicity of Mg is lower than Na and the degree of covalency in the clay-cation relationship is lower for Mg than for Ca (Marchuk and Rengasamy, 2011). It is clear that there are numerous mechanisms affecting the extent of Mg effect, although the common agreed point is that the effect of Mg is clearly not equivalent to Ca – where *not-equivalent* refers to a Mg system with lower stability than for a Ca system under the same conditions. This confirms that the assumption of Mg and Ca being equivalent in effect, as stated in the classical sodium adsorption ratio function of US Salinity Laboratory Staff (1954), is clearly not so.

The findings of this thesis also suggested Mg was not as effective as Ca in maintaining soil structure, although it is pertinent to specifically note that as an individual ion, Mg itself caused extremely negligible clay dispersion (turbidity<15 NTU, which is effectively stable) without external mechanical force or changing pH. For example, Mg saturated soil clays were found in close agreement but consistently not as effective as Ca saturated ones. For a colloidal system at neutral pH:

i) Mg clays always had greater dispersed clay (%) than Ca clays;
ii) The negative charge of Mg clays, as indicated by zeta potential, was consistently more negative than Ca dominant ones;
iii) Mg clays had lower mean particle size than Ca clays at equivalent conditions; and,
iv) The CFC, and subsequent calculations for ionicity and degree of covalency, suggest flocculation and negligible dispersion caused by Mg, especially when compared to Ca calculations for the same.

Additionally, for an aggregated system at neutral pH:

i) Mg aggregates consistently has a lower hydraulic conductivity than Ca aggregates, but did not disperse;
ii) When leached with deionised water, neither the Mg nor Ca system spontaneously dispersed;
iii) Switching a Mg dominated aggregate system from leaching with Mg dominant solution to Ca dominant resulted in improved hydraulic conductivity (reversibility); and,
iv) The addition of mechanical energy to cause dispersion of the aggregated system resulted in both Ca and Mg systems dispersing, with the Mg system settling slower, but eventually settling (supported by zeta potential results).

For both the colloidal and aggregated systems these results support a disaggregation process (expansion of clay domain without dispersion), rather than a dispersion process. In particular, the zeta potential results remaining in an unstable suspension range (stable soil range), and the observed reversibility of the hydraulic system, clearly demonstrate that the soils should be expected to remain stable. Whilst soil stability in terms of an aggregated state was maintained, there was also a clear hydraulic decline. This is the effective definition of disaggregation, as described by Bennett et al. (2019) based on the work of Quirk and Schofield (1955) and McNeal and Coleman (1966). In this circumstance the clay domain expands due to montmorillonite intra-crystalline swelling (where montmorillonite is present) and due to the inter-crystalline swelling brought about by the diffuse double layer development and expansion with lowering in the attractive potential (all soils), including the effects of lowering the degree of covalency. Subsequently, disaggregation operates also as a function of the solution salinity, and a dynamic aggregation-dispersion boundary exists for the soil in terms of the exchangeable-solution cation suite equilibrium and the solution salinity (Bennett et al., 2019; Dang et al., 2018c). It is conceded that negligible dispersion was still observed for the Mg systems investigated, but that this would be considered in the stable range (Zhu et al., 2016). Such dispersion is likely explained by the clay particle size and the resultant interacting charge within the domain, whereby a smaller particle would require lower changes in energy to dislocate individual clay particles from the domain (Bennett et al., 2019; Quirk, 2001). Such a result should also explain why we should never expect the hydraulic conductivity of a system to be completely reversible, but should expect a level of reversibility.

The definition of the specific-effect of Mg as decreasing in hydraulic conductivity and (sometimes) structural stability is ambiguous, as slaking, dispersion and disaggregation all contribute to structural instability. Therefore, we suggest using a clearer definition in describing the effect of Mg on soil structural stability. It is postulated that the term ‘specific’ was used to mean the individual, or direct, effect of Mg, which is currently causing confusion with soil specific effects. It is also pertinent to define this individual, or direct, effect of Mg in terms of the dominant action, which is a change in the pore geometry without dispersion caused by disaggregation, rather than dispersion. In this thesis, soils leached with Mg solutions showed lower K_{sat} than soils leached with Ca solutions, irrespective of soil mineralogy, which further demonstrates the general nature of the disaggregation effect. On this basis, and with support from the evidence above, it is concluded that the reduction of K_{sat} in Mg systems without any dispersion supports the clay domain remaining non-dispersive, but with greater disaggregation due to enhanced inter-crystalline and intra-crystalline swelling. Therefore, it is suggested that the dominant individual, or direct, effect of Mg on soil structural stability is disaggregation.

Such a definition should replace the ambiguous specific-effect of Mg definition that is easily misconstrued, and often misunderstood.

7.1.2. The management of magnesic soil and water sources

Different indices and guidelines have been generated and used in order to predict soil structural degradation and to assist with the management of soil structural maintenance. In terms of the management of magensic soils, there are some suggestions based on the findings from this thesis.

7.1.2.1. Considerations for strategic selection of irrigation water

In Australia and New Zealand, the ANZECC (2000) guidelines are currently used in terms of the appropriate selection of saline-sodic water to maintain soil permeability. This guideline is based on the threshold electrolyte concentration (C_{TH}) concept using the SAR and EC to predict soil structure stability in relation to the irrigation water. The C_{TH} defines a measureable departure from a Ca dominant stable state, whereby this departure is defined as a reduction in K_{sat} (permeability decrease of 10–20%) (Bennett et al., 2019; Bennett and Raine, 2012; Dang et al., 2018d; Ezlit et al., 2013; Quirk and Schofield, 1955). While the ANZECC (2000) guidelines provide a generalised relationship, whereby if the values of SAR and EC for a given quality of water for irrigation fall on the right side of the dashed line Figure 2-11 in this thesis (Figure 4.2.2 in ANZECC 2000), the irrigation water can be safely used without detrimental impact on soil structure, it has been unequivocally demonstrated that the C_{TH} is a soil-specific phenomena (Bennett et al., 2019). In contrast, if the values of EC and SAR fall to the left side of the solid line, this water is likely to have detrimental effect on the soil structure. In addition, for those values of EC and SAR falling in between of the two lines, the structure change depends on soil property and rainfall and it requires careful consideration of management. Ezlit et al. (2013) developed a disaggregation model to semi-empirically determine the C_{TH} to address this soil-specificity, although the inclusion of Mg in this model has not yet been achieved (Bennett et al., 2019).

This thesis has established that Mg has a differential effect, as compared to Ca, and the literature demonstrates that K behaves differently to Na (Dang et al., 2018b; Marchuk et al., 2016; Marchuk and Marchuk, 2018; Rengasamy and Marchuk, 2011), in terms of soil structural stability. The CFC work in Chapter 6 demonstrates the soil-specific effect of Mg on the physicochemical mechanisms governing soil stability. This demands consideration, then, in the C_{TH} disaggregation model (Ezlit et al., 2013). Dang et al. (2018b) sought to incorporate K into the disaggregation model and concluded that the apparent coefficient of equivalence, 'a' – transforming the K concentration into an equivalent Na concentration – changed with time, and postulated this could be due to illitisation (Marchuk et al., 2016), even though the system did not undergo periods of drying. The result of their work suggested that inclusion of the $a[K]$ term in Equation 7.1 is reasonable:

$$Na_T = [Na] + a[K] \qquad \text{Eqn. 7.1}$$

where Na_T is the total Na effectiveness, a is the coefficient of equivalence and [Na] and [K] terms are in $\mathrm{mmol_c/L}$. This equation was reasonable defined as the fact that inclusion would remain conservative in favour of the environment, meaning that the semi-empirical model advice on water quality suitability will always provide a recommendation that is more conservative than the true C_{TH}, including the a[K] term, is likely to be. The sensitivity analysis for c[Mg] within the EDP suggests that inclusion of Mg in the dispersive numerator is likely not warranted, as even in extreme cases the impact of this term is minor, and physically unlikely to be important. On the other hand, inclusion of the b[Mg] term is warranted and could be considered as Equation 7.2:

$$Ca_T = [Ca] + b[Mg] \qquad \text{Eqn. 7.2}$$

where Ca_T is the total Ca effectiveness, b is the coefficient of equivalence and [Ca] and [Mg] terms are in $\mathrm{mmol_c/L}$. However, this needs to be validated, especially as Mg has multiple mechanisms for affecting structure beyond the ionicity concept (see: Section 7.1.1.6).

The experimentation in this thesis suggests that attention must be paid to the selection of a proper baseline solution because large differences may occur when the concentration varies. Quirk and Schofield (1955) used 0.0316 M $MgCl_2$ solution as a baseline for magnesium-saturation and 0.01 M $CaCl_2$ solution for calcium-saturation. However, these two baseline concentrations may not necessarily have provided the greatest K_{sat}, as our study indicated that the greatest K_{sat} for Mg and Ca saturated soils depended on soil mineralogy and texture. For example, in the Urrbrae soil, choosing a baseline solution between 0.01 M and 0.25 M $MgCl_2$, the K_{sat} can vary by 47%, which was much greater than the C_{TH} definition of 20% reduction in K_{sat} (Ezlit et al., 2013). On the other hand, the practicality of the C_{TH} method needs to be considered. In selecting a baseline condition based on electrolyte concentration, the field condition needs to be considered. Should the baseline be an arbitrarily high concentration to measure absolute stability, or should it reflect a reasonable range of concentration likely to be physically encountered in the irrigation circumstance? The former could result in undue underutilisation of marginal irrigation water on a strategic basis, whilst the latter reflects the reasoning of a potential minima being important to the determination of structural decline (Quirk, 2001). Due to the former reasoning, the Ezlit et al. (2013) disaggregation model uses fixed electrolyte concentrations within a physically possible range for irrigation. Irrespective of these aspects, the notion of the potential minima occurring as absolute stability in an essentially pure Ca system is called into question; further work needs to determine the importance of this state to the physical mechanisms of the system and the practicality of an irrigation guideline.

Thus, there is a clear requirement to consider the role of Mg in the selection of irrigation water suitability for strategic irrigation. The baseline solution needs to be considered in terms of the physical meaning and practical importance, while incorporation of Mg effects within the disaggregation model, and subsequent applicability of irrigation suitability recommendations, requires validation. Future guidelines for assessing structural stability dynamics would do well to ensure that the effect of Mg, and K for that matter, is incorporated to truly ensure soil security and production longevity for generations to come.

7.1.2.2. Optimization of CROSS and EDP as soil structural stability metrics

In agriculture, the prediction of soil clay dispersion is critical for land management. Traditionally, determining an amendment strategy for sodic soil relies on the measurement of SAR or ESP, in conjunction with the EC, to decide the amount and type of amendment material. As CROSS and EDP indices have incorporated the effects of Mg and K, these indices were used to predict soil structural stability in this thesis, and should be considered as superseding both he SAR and ESP, respectively. Ten contrasting soils, with varying pH and clay minerals, underwent a mechanical dispersion test as part of the development of a dispersed clay quantitative methodology (Zhu et al., 2016). A strong relationship (R^2=0.771) was found between mechanically dispersed clay and variables, including EC, EDP and clay content. Similarly, a strong relationship (R^2=0.705) was found between mechanically dispersed clay and CROSS in conjunction with EC. However, using CROSS and EDP as sole predictive indices didn’t improve the prediction level significantly. This suggests that there are other factors controlling stability, but was also motivation for subsequent investigation into the use for soil-specific coefficients *a*, *b* and *c* in CROSS and EDP. Smith et al. (2015) have demonstrated that the coefficients can be optimized, which the results in this thesis support based on the fact these coefficients are soil-specific with coefficients *a* and *b* having the greatest influence. This thesis have confirmed that due to the variance of coefficients of Mg and K, the CROSS_{spc} and EDP_{spc} can be largely different from the generalised CROSS and EDP. Further research is recommended to verify the CROSS_{spc} and EDP_{spc} in predicting clay dispersion.

It is agreed that there are other factors governing clay dispersion in the system, although it is pertinent to also consider how the results from this thesis can be used to improve stability metrics. The major result of this body of work is the determination from both colloidal and aggregated systems that the primary, and clearly dominant, role of Mg in soil structural stability is disaggregation. Hence, the Mg function is one with greater contribution to the stability condition, rather than the instability condition. This further confirms the assertions of Curtin et al. (1994b) and He et al. (2013) that dispersion in a soil systems containing Na is enhanced in the presence of Mg, on the basis that Mg increases disaggregation through a larger diffuse double layer and lower degree of covalency. Importantly, this is not a direct Mg effect on dispersion, but an interacting effect with Na. We suggest that the interacting effect is likely with monovalent ions in general, not just Na. Therefore, in terms of EDP and CROSS, we might expect improvement in the formulae, and subsequent predictive capability of these, through the following modification:

$$EDP = \left[\frac{([Na] + a[K])d_{Mg}}{CEC}\right]100 \qquad \text{Eqn. 7.3}$$

and,

$$CROSS = \frac{([Na] + a[K])d_{Mg}}{\sqrt{0.5([Ca] + b[Mg])}} \qquad \text{Eqn. 7.4}$$

where all concentrations are cmol_c/kg for EDP and mmol_c/L for CROSS, and the terms in both EDP and CROSS are the same, except for the inclusion of d_{Mg}. The d_{Mg} term provides the means to include an interaction effect of Mg with the monovalent ions that enhances their effect based on the presence of Mg ($d_{Mg} \geq 1.0$). While this is a reasonable modification, it is completely theoretical and requires substantial investigation over a large number of soils. It is acknowledged that the effects of Mg and K on soil structural stability are likely to differ between mixed cation system and homoionic systems due to demixing (Nelson et al., 1999). These may have implications for the coefficients and term d_{Mg} used in EDP and CROSS for soils in their natural (mixed cation) state. It is suggested this term d_{Mg} will also exhibit as soil specific, and be non-linear in nature. This supports the judicious use of machine learning approaches where the results can be interrogated for uncertainty (*i.e.* not a "black box" approach). In terms of the management of magnesic soils and water sources, it will be pertinent to consider how this interaction effect manifests, as well as its magnitude.

7.1.2.3. Naturally occurring magnesic soils

There is an overwhelming body of work on sodic soils, with modern nomenclature moving towards dispersive soils as the general term. However, there is a complete paucity of literature pertaining to naturally occurring magnesic soils and the consequence of these in terms of soil structure and subsequent system function. Soils that are magnesic by definition of the Australian Soil Classification (Isbell, 1997; 2016) are particularly hard to source, as was discovered in the undertaking of this body of work. While this suggests that the occurrence of such soils is rare, there is a vast quantity of soils in Australia (*e.g* Hillston irrigation regions through to the Hay Plain, and Central Queensland) where Mg dominates the CEC (Dr Pat Hulme and Dr Andrew Biggs, pers. comm. 2018), although the extent of these is not well established. How these soils function in the natural environment, their inherent constraints, and the interaction of these constraint with other constraints within the production system is not well understood. It is therefore recommended that such soils are investigated in terms of the conclusions of the experimental conclusions of this thesis. Furthermore, it would be pertinent to conduct a level of land survey involving the extent of magnesic soils throughout Australia; the data for this should largely be available in Government databases.

7.2. Conclusions

With regard to the using a turbidimeter for quantifying dispersed clay, some conclusions are drawn:

- The linearity of turbidity by dilution was verified, by considering the effects of soil colour and mean particle size.
- Strong correlation between turbidity (NTU) and dispersed clay (mg/L, % of soil) was found for each soil.
- The use of a turbidimeter for quantifying clay released from soil was validated. The coefficients between turbidity and dispersed clay were very close for 9 soils with an average coefficient of 0.677. The average of the coefficients was further used to generate a general equation converting turbidity to dispersed clay. Consequently, the

dispersed clay can be accurately and quickly calculated by using a turbidimeter after spontaneous and mechanical dispersion tests.

With respect to the effect of magnesium on soil structural stability, the following conclusions are drawn:

- The effect of Mg in causing soil clay dispersion was negligible, as compared to Na. Through leaching a wide range concentration of Mg solution on contrasting soils, no visual dispersion was observed in the leachate. Subsequently, when magnesic soil was leached with deionised water, only negligible turbidity from the leachate was detected (turbidity<15 NTU). The aggregate stability test further confirmed that effectively nil dispersion occurred in magnesic soil aggregates.
- The major role of Mg is aiding/maintaining soil structural stability. With changing pH, the negative charge (zeta potential) of Mg soil clays was greater than -30 mV, which indicated that Mg soil clays are prone to flocculate.
- However, Mg was not as efficient as Ca in aiding/maintaining soil structural stability. Mg had a disaggregation effect on soil structural stability by reducing K_{sat} and dissolving more DOC. These were related to Mg induced disaggregation due to intra-crystalline swelling in montmorillonite clay and/or diffuse double layer development driven intre-crystalline swelling when electrolyte concentration decreases, or Mg relative-concentration increases. Furthermore, Mg clays showed more net negative charge (ζ-potential) and lower mean particle size than Ca dominant ones at similar conditions, irrespective of clay mineralogy and soil pH. The difference between Mg and Ca on clay dispersive behaviour, although both being divalent cation, is also related to the fact that Mg has a lower degree of covalency bonding to clay than that of Ca.
- With external mechanical force, Mg soils showed higher dispersed clay than for an equivalent Ca system, although Mg soils eventually flocculated. The dispersed clays in the Mg system required a longer time to settle than that of Ca dominant system, which may be related to smaller mean particle size of Mg-dominant clays than Ca-dominant clays. Attention should be paid to this phenomena, as it could cause surface sealing when magnesic soils suffered mechanical force.

- Clay mineralogy has an impact on the effect of Mg on clay dispersion, particularly when soil pH is changing, and/or involved with external force.
- The effect of Mg on structural stability is soil specific, evidenced by its varying flocculative coefficients and dispersive coefficients within a range of soils. This can be related to soil mineralogy and co-existing material, *e.g.* organic matter and oxides.
- The individual/direct effect of Mg on soil structural stability has been redefined as a disaggregation effect, rather than a specific-effect described by reduction in hydraulic conductivity and dispersion.

7.3. Future research directions

Based on the outcomes from this thesis, the following future work is recommended:

- In this research, the ionicity index of Na, K, Mg and Ca showed strong correlation to the dispersive behaviour of each homoionic soil clay, including the dispersed clay percentage, zeta potential and mean particle size. The disaggregation effect of Mg as compared to Ca on soil structural stability was demonstrated in the reduction of K_{sat} and dissolving more organic matter from clay surface. However, all the treatment solutions in either soil clay suspension or soil aggregates system were using Cl^- as the balancing anion. Future research is recommended to investigate the effect of Mg in conjunction with different anions, *e.g.*, Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-, as treatment solutions for soil structural stability investigations, and in the investigation of the applicability of CROSS and EDP. It is expected that the effect of Mg could behave differently in a Cl^- system as compared to other anion systems. In general, specific cation effects are less pronounced than specific anion effects, because anions have stronger interactions with water than cations of the same size and absolute charge density. Only when direct ion–ion or ion–clay interactions are dominant, specific cation effects can be of the same order of magnitude as specific anion effects (Kunz, 2010). Furthermore, these anions possess different abilities in dissociating in aqueous solution to provide H^+ and/or OH^- (Myers, 2003), which may further alter the pH within the soil. Hence, future research is recommended in studying soil structural stability of magnesic soils in various anion systems. The results would certainly be beneficial for practical management.

- Many irrigation guidelines are based on the C_{TH} concept to avoid the adverse effects on infiltration in unstable soils (Jayawardane, 1979; Quirk and Schofield, 1955; Rengasamy et al., 1984). However, the majority research of C_{TH} is based on Na-Ca system. In this research, Mg had been found less efficient in aiding flocculating as compared to Ca, and its effect varies in terms of soils (soil specific). Thus, it is important to determine the C_{TH} curves when Mg is used as the counter ion to Na (and/or K), and compare the results to that of Ca system. In return, the study can provide valuable information in completing the C_{TH} disaggregation model. The incorporation of the effect of K and Mg into C_{TH} models can also increase its reliability. The baseline conditions and the applicability of a potential minima in an effectively pure Ca system should also be further investigated in terms of both the physical mechanisms, and the practical implications of these.
- In this thesis, the dispersive coefficient of K and Mg, as well as the flocculative coefficient of Mg, was examined using the flocculating power of Na, K, Mg and Ca, based on CFC method in 17 soils. This was the same method used by Rengasamy and Sumner (1998). In this way, the results obtained from this thesis can be easily compared to the values obtained from Rengasamy and Sumner (1998). CFC values define the minimum concentration to flocculate a given amount of clay in a fixed time. In comparison, the point where turbidity (clay dispersion) is first observed in a leachate was defined as turbidity concentration (C_{TU}) by Quirk and Schofield (1955), or the aggregation-dispersion boundary condition (Dang et al., 2018c). It is of great interest to determine the C_{TU} for the 17 soils, and compare the derived coefficients from C_{TU} study to these obtained from CFC study. However, running C_{TH} and C_{TU} with Na, K, Mg and Ca mixed cation system can be even more time-consuming than traditional C_{TH} method. Thus, a better and easy-operating method to analyse C_{TH} and C_{TU} is required.
- The general discussion of this thesis has presented modified EDP and CROSS formulae based on the inclusion of a d_{Mg} term that allows accounting for an interaction effect between Mg and monovalent cations in the prediction of soil structural instability; where $d_{Mg} \geq 1.0$ and enhances the monovalent ion effect. This has not been experimentally validated and should be. Furthermore, there is merit in obtaining a large dataset of numerous soils of varying attributes and geospatial origin to seek to determine the soil specificity of EDP and CROSS factors, as well as the likely magnitude of soil-specificity that the d_{Mg} term possesses.

- Due to limited distribution and information pertaining to naturally magnesic soil, Mg affected soil in this research were artificially treated. This provided advantages in selecting contrast clay mineralogy and controlling soil pH, but came with the disadvantage of not being a naturally occurring soil system. It would be very interesting, and pertinent in terms of particle management guidelines, to locate natural magnesic soils and generate a data source of soil physical and chemical properties, preferably related to yield data if possible. On one hand, these soils could be used to verify the CROSS and EDP concept in predicting soil structural stability. On the other hand, through soil property analysis and amendment application, the plant yield could be monitored over time and contribute to the formulation and verification of management strategies in a practical sense. It is suggested that much of this information will exist with Government agencies (likely not related to yield data, however), although has not been interrogated for such a purpose.
- To better understand the behaviour of soils in contact with differing solution concentrations, or changes in the electrolyte suite composition, there is requirement to understand the meso- and micro-structure (main functional pore sizes at field condition) dynamics throughout the leaching period. The pore sizes are usually in a range of several nanometres to hundreds of micrometres. Traditional measuring technologies for pores, such as gas absorption techniques, or mercury intrusion porosimetry, usually require drying procedures to remove water. This drying process permanently alters the real situations of the pore, and does not facilitate continuous measurement of subsequent solution changes on the one sample. Thus, the results cannot reflect the aggregation of clay particles and other fines within a dynamic system. Nuclear magnetic resonance (^{1}H NMR) has the advantage of in-situ measurement. The application of NMR spin–lattice relaxation measurements of water or concentration solution or other liquids contained in a porous solid provides a suitable tool for the determination of pore size distributions. Other advantages of NMR methods over conventional porosimetry/adsorption techniques include the study of wet solids, a wide range of sample sizes, and no pore shape assumption required. In principle, water contained in different sized pores will have different the transversal relaxation time (T_2). The sample can be a tube in diameter of 2–8 cm and given height, in this format, the leaching water can be applied directly and tested immediately at different intervals or by changing the leaching solution. Additionally, computer tomography scanning techniques have

successfully been applied to determine soil pore connectivity and function, allowing a dynamic model specific to the soil sample in question to be developed. Investigation of such techniques in relation to solution changes and structural dynamics is highly recommended. Correlating the pore dynamic information and the composition of cations and mineralogy of soils with their permeability and flocculation will give an invaluable insight for soil physical and physiochemical properties, leading to great advances in a functional model for soil genesis and dynamic structure.

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Appendix

A.1 The visual changes in homoionic soil clays at changing pH

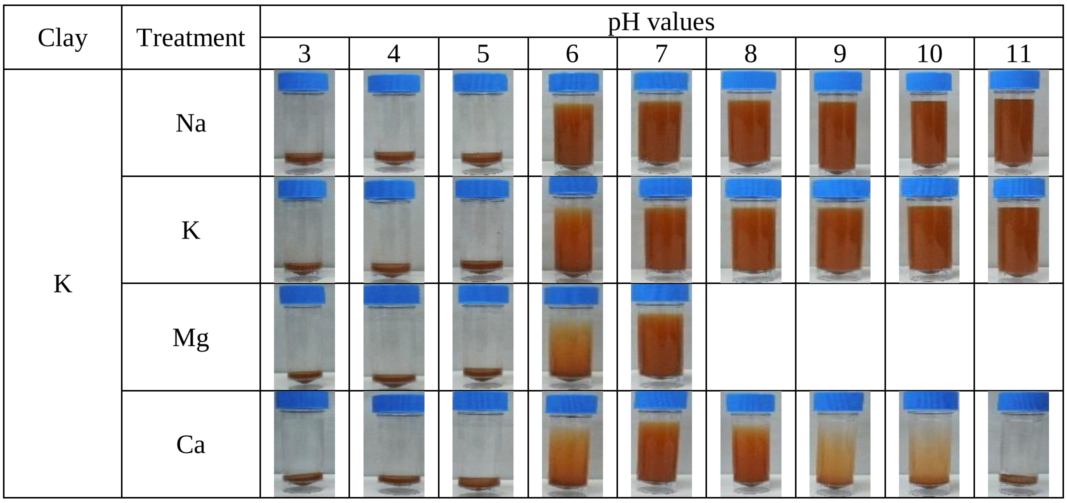


Fig. 0–1 The visual changes in dispersive behaviour of Na, K, Mg, Ca kaolinite soil clays at pH 3 to pH 11.

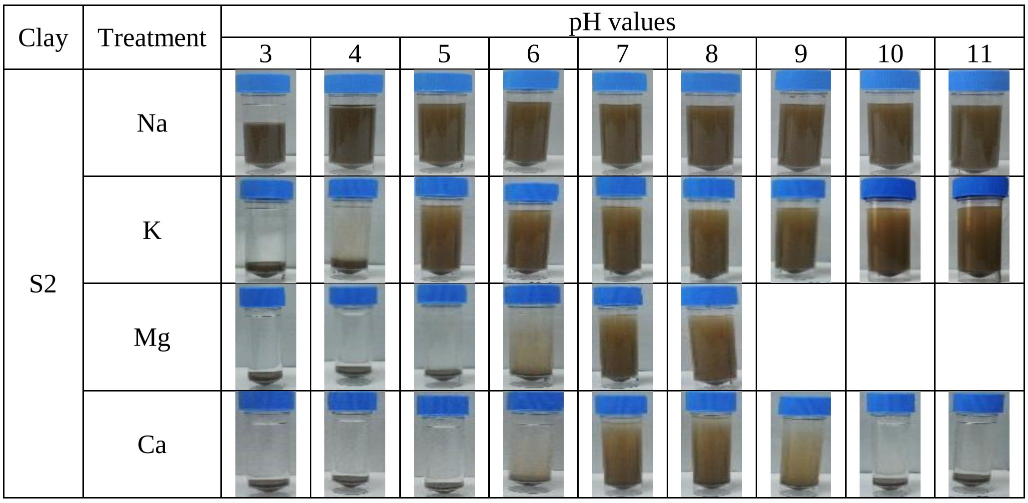


Fig. 0–2 The visual changes in dispersive behaviour of Na, K, Mg, Ca montmorillonite soil clays at pH 3 to pH 11.

Clay	Treatment	pH values								
		3	4	5	6	7	8	9	10	11
S3	Na									
	K									
	Mg									
	Ca									

Fig. 0–3 The visual changes in dispersive behaviour of Na, K, Mg, Ca homoionic illite soil clays at pH 3 to pH 11.

A.2 The exchangeable cation percentage of four soils after each treatment

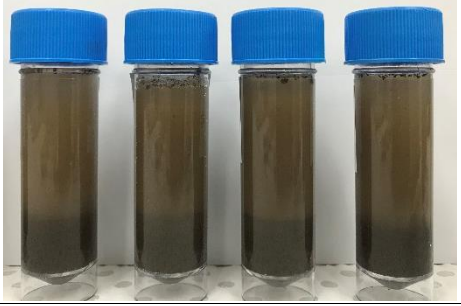
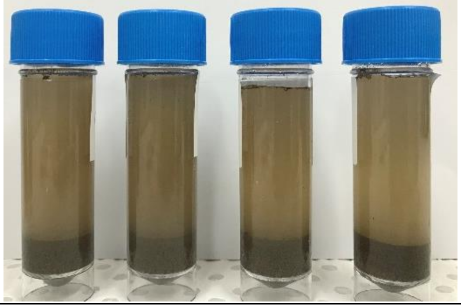
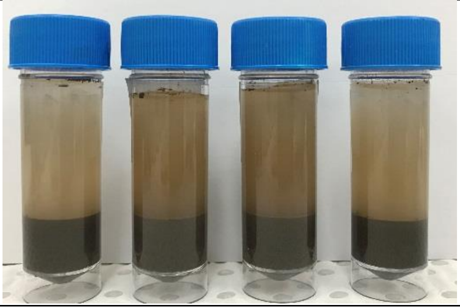
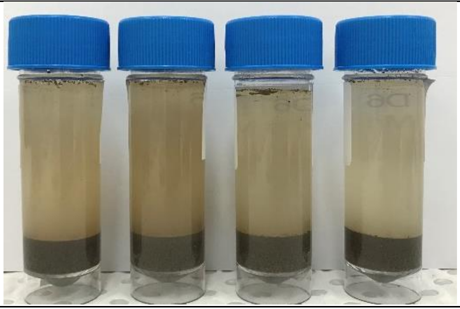
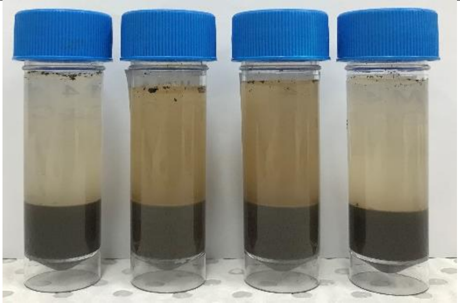
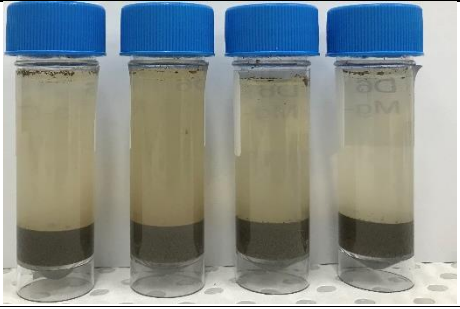
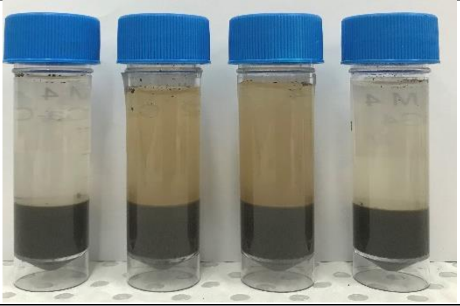
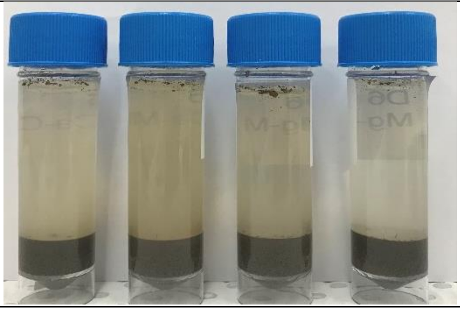
M4 soil after each treatment solution	G1 ECP	G1 EMP	G2 ECP	G2 EMP	G3 ECP	G3 EMP	G4 ECP	G4 EMP
0.5 M	98.01	0.92	98.16	0.82	1.05	98.00	0.56	98.53
0.25 M	97.73	1.07	1.22	97.64	0.48	98.44	97.73	1.17
0.1 M	97.71	1.07	0.57	98.29	0.36	98.67	97.92	1.03
0.05 M	97.71	1.08	0.45	98.44	0.33	98.37	97.79	1.07
0.025 M	97.60	1.10	0.61	98.11	0.53	97.76	97.80	1.07
0.01 M	97.42	1.15	0.67	97.81	0.54	98.10	97.56	1.17
0.005 M	97.30	1.24	0.85	97.77	0.50	98.01	97.53	1.19
0.001 M	97.18	1.39	1.04	97.61	0.60	97.89	97.07	1.49
0.0001 M	96.59	1.86	1.12	97.53	0.63	97.82	96.54	1.87
DI	96.06	2.14	1.36	97.12	0.68	97.66	95.99	2.21

D6 soil after each treatment solution	G1 ECP	G1 EMP	G2 ECP	G2 EMP	G3 ECP	G3 EMP	G4 ECP	G4 EMP
0.5 M	98.92	0.31	98.73	0.34	3.29	95.75	2.90	94.37
0.25 M	97.60	1.38	3.65	94.01	1.85	97.02	97.68	1.50
0.1 M	97.75	1.33	2.03	96.04	2.01	96.96	98.99	0.32
0.05 M	97.85	1.06	2.18	96.27	2.54	96.51	98.93	0.29
0.025 M	97.62	1.12	2.27	96.18	2.23	96.73	98.69	0.34
0.01 M	97.34	1.14	1.95	96.35	2.48	96.46	97.67	1.34
0.005 M	97.21	1.19	2.26	95.80	3.01	95.58	97.35	1.44
0.001 M	96.99	1.17	3.58	94.56	3.50	94.73	96.85	1.60
0.0001 M	96.53	1.54	3.51	94.42	3.99	94.25	96.02	2.01
DI	96.04	1.85	3.53	94.31	4.48	93.53	95.63	2.31

Urrbrae soil after each treatment solution	G1 ECP	G1 EMP	G2 ECP	G2 EMP	G3 ECP	G3 EMP	G4 ECP	G4 EMP
0.5 M	95.45	2.53	95.85	2.25	4.73	90.84	3.40	91.94
0.25 M	95.69	2.43	4.10	91.77	4.24	91.34	95.20	2.74
0.1 M	95.57	2.29	2.67	93.88	3.36	92.98	95.46	2.36
0.05 M	95.60	2.27	2.70	93.90	3.25	93.02	95.40	2.30
0.025 M	95.31	2.50	2.75	93.71	3.34	92.99	95.03	2.51
0.01 M	95.18	2.68	2.87	93.48	3.40	92.95	94.53	2.66
0.005 M	94.96	2.77	3.09	93.37	3.44	92.88	94.61	2.73
0.001 M	94.67	2.92	3.51	93.01	3.52	92.76	94.48	2.99
0.0001 M	94.52	2.96	3.99	92.55	3.89	92.41	94.22	3.15
DI	94.34	3.05	5.24	91.25	4.40	91.84	93.91	3.34

Timberlea soil after each treatment solution	G1 ECP	G1 EMP	G2 ECP	G2 EMP	G3 ECP	G3 EMP	G4 ECP	G4 EMP
0.5 M	91.35	5.61	91.71	5.37	1.70	92.98	2.66	93.10
0.25 M	92.61	4.85	3.18	93.09	2.00	93.55	91.28	5.60
0.1 M	92.47	4.75	1.14	96.31	1.48	93.53	93.10	4.30
0.05 M	92.45	4.72	1.25	96.20	1.45	93.55	93.30	4.10
0.025 M	92.20	4.96	1.46	95.35	1.66	93.43	93.07	4.56
0.01 M	92.03	5.29	1.89	94.94	1.69	93.38	92.34	5.70
0.005 M	91.82	5.63	1.88	95.08	1.74	93.30	92.46	5.65
0.001 M	91.25	6.21	1.90	95.07	1.79	93.37	92.42	5.76
0.0001 M	91.51	6.08	1.94	95.26	2.03	93.31	92.30	5.91
DI	91.59	6.34	1.93	95.32	2.22	93.28	92.16	6.04

A.3 Mechanical dispersion assessment

M4 soil (montmorillonite)				D6 soil (montmorillonite)			
G1	G2	G3	G4	G1	G2	G3	G4
Mechanical dispersion 4 hrs				Mechanical dispersion 4hrs			
							
Mechanical dispersion 24 hrs				Mechanical dispersion 24 hrs			
							
Mechanical dispersion 48 hrs				Mechanical dispersion 48 hrs			
							
Mechanical dispersion 72 hrs				Mechanical dispersion 72 hrs			
							

<table>
<tr><td colspan="4">Timberlea soil (kaolinite)</td><td colspan="4">Urrbrea soil (illite)</td></tr>
<tr><td>G1</td><td>G2</td><td>G3</td><td>G4</td><td>G1</td><td>G2</td><td>G3</td><td>G4</td></tr>
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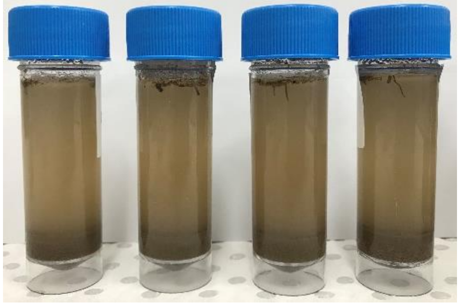
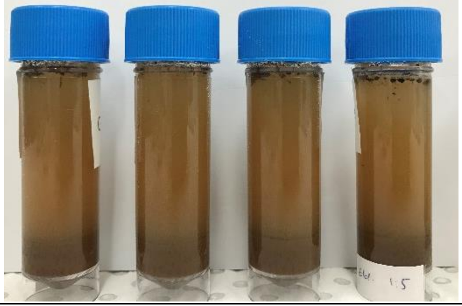
<tr><td colspan="4"></td><td colspan="4"> </td></tr>
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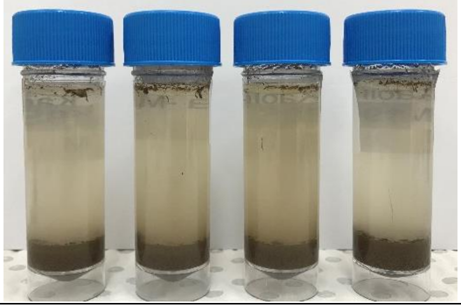
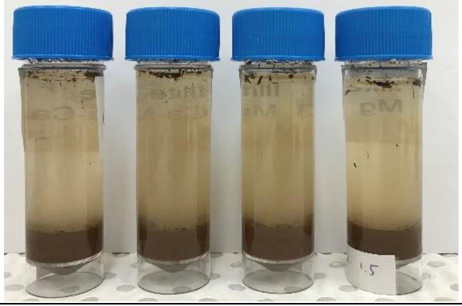
<tr><td colspan="4"></td><td colspan="4"> </td></tr>
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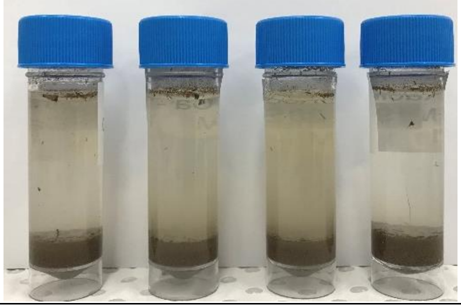
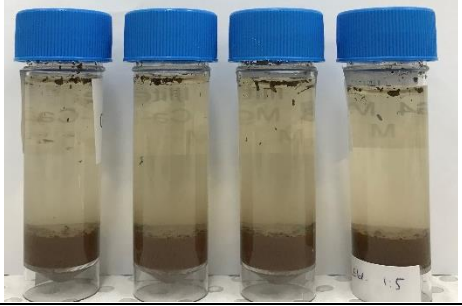
<tr><td colspan="4"></td><td colspan="4"> </td></tr>
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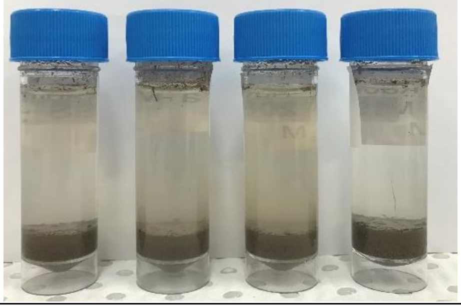
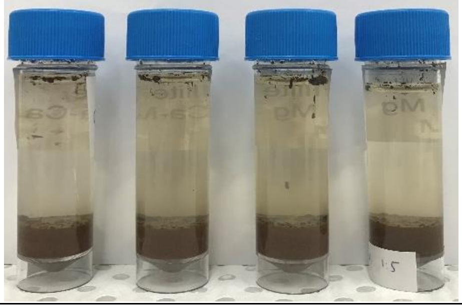
<tr><td colspan="4"></td><td colspan="4"> </td></tr>
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