

SODIC SOIL SWELLING AND DISPERSION AND THEIR IMPLICATIONS FOR WATER  
MOVEMENT AND MANAGEMENT

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**Title**  
SODIC SOIL SWELLING AND DISPERSION AND THEIR  
IMPLICATIONS FOR WATER MOVEMENT AND MANAGEMENT

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**DOCTOR OF PHILOSOPHY**

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## ABSTRACT

North Dakota has over 1.9 million ha of sodium-affected soils, influencing water movement and crop production. This dissertation consists of four studies examining different aspects of sodic soils. The first study surveys sodium adsorption ratio (SAR) methods to determine which is the most reliable. The second and third studies investigate the dispersion and swelling functions of sodic soils. The final study examines field spatial distribution of Na in order to propose management strategies.

Analytical approaches for converting alternative to standard approaches are needed. The SAR was determined from many non-standard techniques. One hundred soils were used, SAR<sub>e</sub> and 1:5 soil/water SAR<sub>1:5</sub> determined using shaking, stirring, and a USDA-NRCS method were compared. Three of the methods influenced the SAR<sub>1:5</sub> values.

Electrical conductivity (EC), SAR, and Ca/Mg ratios influence dispersion. Three pure clay minerals (montmorillonite, kaolinite and illite) were pretreated by variable Na and cation ratios and absorbance was determined using spectrophotometer for dispersion. Calcium-Mg ratios across the same SAR did not influence clay dispersion. Dispersion increased with higher SAR and reduced EC whereas no dispersion for kaolinite.

Swelling is associated with hydration of clays, which forces clay tactoids to separate. Four soil series from North Dakota field sites were used. To assess swelling, field capacity (FC) was used as proxy. The study found that soil Na and soluble salt concentrations were two important chemical factors influencing FCW. The FCW increases with increased SAR and lower levels of EC. These results indicate that maintaining an EC level above 4 dS m<sup>-1</sup> may mitigate swelling, which is an issue considered in tile drainage.

Over- and under-application of amendments in sodic soils was studied in a 8.1 ha sodic soil field. At each site, samples were taken from two depths; electromagnetic (EM38) and elevation readings were done. Elevation was significantly correlated with soil variables except for Na%. The EM38 was reliable to express soil EC and was correlated with Na% and dispersion. Therefore, conducting the EM38 and RTK may allow site-specific management of Na. Improved knowledge of sodic soils dispersion, swelling, and field distribution will benefit researchers and farmers in managing their fields.

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I am very grateful to my families for their support of my further education and for their love and encouragement in my life.

## **DEDICATION**

To my father Jinlong He and grandmother Qing Yu, for what they had done, the great love they had given to me, and the great lessons they had taught me in my life.

## PREFACE

This dissertation consists of eight parts that include a general abstract, general introduction, literature review, one published paper, and three manuscripts that will be submitted for publication in appropriate scientific journals, and a general conclusion. The general abstract is a brief description of the outline of research. The general introduction provides an understanding of the importance of this study, and how all research studies are related to the main issue: sodic soil characterization and its effect on water movement. The literature review introduces the development of sodic soils and their significant distribution in North Dakota, discusses the factors influencing sodic soil dispersion and swelling, and the adverse effects on crops and tile drainage, and land management. The first paper investigates a relationship between  $SAR_{1:5}$  and  $SAR_e$  under different methods. The second paper discusses how EC, SAR, and Ca/Mg ratios affect clay dispersion. The third paper presents how different chemical factors affect the swelling of sodic soils. The fourth paper investigates the spatial distribution of sodic soils in a field-based study to provide a template for precision management. Finally, the general conclusions from all research studies are presented. References are listed at the end of each part of the dissertation except for the general introduction and conclusion.

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## GENERAL INTRODUCTION

Excessive levels of salts occur in large soil areas around the world and affect land use. Soils that are dominated by sodium salts are classified as “sodic”. Traditionally, US sodic soils are characterized by E<sub>Ce</sub> values  $< 4 \text{ dS m}^{-1}$ , exchangeable sodium percentage (ESP)  $> 15$ , saturated paste extract sodium adsorption ratio (SAR<sub>e</sub>)  $\geq 13$ , and  $\text{pH} > 8.5$  (U.S. Salinity Laboratory Staff, 1954). Globally, sodic soils are the largest proportion of salt-affected soils, representing 581.0 million ha of total 932.2 million ha of salt-affected soils (Szabolcs, 1989; Sumner and Naidu, 1998). Sodic soils occur in many areas of the Northern Great Plains, and in North Dakota alone, sodium affects more than 1.9 million ha.

Sodium-affected soils are markedly unproductive for both crop and rangeland and also lead to land degradation (Jayawardane and Chan, 1994; Qadir and Schubert, 2002). The sodic horizon restricts the movement of water, decreases soil water hydraulic conductivity (K<sub>sat</sub>), and inhibits plant root penetration. These adverse effects are related to the factors that control soil swelling and dispersion (So and Aylmore, 1993; Sumner and Naidu, 1998). Swelling and dispersion are the major mechanisms that cause soil structure deterioration when sodium is present (So and Aylmore, 1993; Sumner and Naidu, 1998). Many farmers have installed tile drainage in North Dakota in recent years to reduce soluble salts and drain excess water due to wet cycle since 1993. But in sodium affected soils, swelling and dispersion may occur when the beneficial cations  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are leached out of soil and  $\text{Na}^{+}$  dominated on the soil exchange sites. This may occur more often if tile is installed below a zone of sodic or saline-sodic subsoils.

Application of chemical amendments is recommended to remediate sodic soils by slightly increasing the salt concentration and increasing the levels of  $\text{Ca}^{2+}$  in sodic soils. However, sodic soils often have high spatial variability at the field scale and sodium-affected soils are often

interspersed with higher-productivity soils (Yang et al., 2011). The heterogeneity of sodicity at the field scale makes site-specific management difficult.

Therefore, to prevent further land degradation and to help provide answers for farmers considering of those that have installed tile in sodic soils, improved knowledge of sodic soil function and theory is needed. This dissertation research was performed to investigate the relationships between SAR methods, characterize the function of dispersion and swelling of sodic soils in pure clay minerals and agricultural field soils, and to investigate the Na distribution with elevation and water flow and soil factors at a field scale research site in order to predict application rates and costs.

## LITERATURE REVIEW

### Sodic Soils Genesis and Terminology Development

Excessive levels of salts in soils occur in large areas around the world and negatively affect land use. Usually, these problematic soils are defined into two major types, namely, saline and sodic. The terms to describe soils that are affected by sodium have varied in soil science history and the first report of “alkali” soils in the United States was made by Hilgard (1877) whose investigations did not consider the influence of chemical reactions and physical properties on soil structure during leaching. Since 1937, different studies demonstrated the importance of electrolyte concentration in maintaining the permeability of soils (Fireman, 1944; Kelly, 1937), and the first attempt of regional definition was made by the staff at the U.S. Regional Salinity Laboratory in California (Kelly, 1951). Subsequently, the nonsaline-alkali soils were defined considering factors of exchangeable sodium percentage (ESP), electrical conductivity (EC), and pH by the U.S. Salinity Laboratory Staff (1954). In 1958, a recommendation was made in the United States to replace the term “alkali” with “sodic” to describe these problematic soils (Bower et al., 1958). Other countries have had similar development of terminology. In the late 1800s, early Russian soil scientists first introduced the term “Solonetz” to distinguish a unique soil distributed in patches in the eastern European plains (Pawluk, 1982). This term is still used in the Canadian soil classification system where a soil may have a solonetz great group (similar to the “natric” great group in US soil classification system), which is designated similar to the term “sodic”. Later, the term “sodic” was widely accepted by the Soil Science Society of America and by 1979 the term “alkali” became obsolete (Soil Science Society of America, 1979).

Sodic soils develop as a result of the stepwise pedogenic processes of salinization, solonization, and solodization (Kellogg, 1934; Sumner and Naidu, 1998). The development

model for sodic soil was established according to the early Russian pedologist, K.K. Gedroiz. By tracing the evolution of the patches of sodic soil, it is possible to understand its development for the morphology patterns (Hopkins, 1989; Schaetzl and Anderson, 2005).

Sodic soils formation was originally attributed to salinization, the buildup of salts (including Na) in the soil. In the dry season, contributing factors are groundwater discharge, i.e. capillary rise of saline groundwater movement, and salts present in parent materials (Sumner and Naidu, 1998). In winter, exclusion of salts in the freezing zone also contribute to salt accumulation as water moves towards the freezing front (Fullerton and Pawluk, 1987). Salt-accumulation progresses as long as the potential evapotranspiration is greater than precipitation, and therefore soluble salts move up into the soil surface and the soil solution becomes concentrated. As a result, divalent cations (mainly Ca) in less soluble minerals such as calcite and gypsum first precipitate in subsoil, and more soluble Na-SO<sub>4</sub> continues to be transported upward and after evaporation precipitates close to the soil surface. As a consequence, Na becomes concentrated in the upper soil horizon (Miller and Brierley, 2011) and the presence of Na facilitates solonization (alkalization).

During solonization salts are reduced dilution by percolating rainwater but Na<sup>+</sup> ions are accumulated on the soil exchange complex of clay minerals, resulting in dispersion of clays when ESP exceeds 10-15 and total salt content is less than 0.10 to 0.15% (1.7 to 2 dS m<sup>-1</sup>) (Miller and Brierley, 2011). During solonization, substantial leaches of dispersed clay eluviates from the surface to subsoil, forming a dense impermeable Btn horizon having a high concentration of clay and Na. As a result, the Btn often has columnar structure and frequently has a rounded-“biscuit” top covered with white powder which is an eluvial E horizon of little sand and silt, precipitated silica, and no organic matter (Miller and Brierley, 2011).

As an important diagnostic property of solonetz soils, the presence of a unique columnar structures was first pointed out by Zemiatchensky in Russia in 1894 (MacGregor and Wyatt, 1945). In the initial stage of this process, translocation of water into the lower soil profile is difficult and follows basically along desiccation cracks because the high concentration of Na (B<sub>tn</sub>) causes the matrix to be impermeable. During the process water leaches through the cracks and clays are degraded and stripped, forming columns in the B horizon. Similarly, the top of columns round to form a “biscuit top” because water strips materials away from the top more easily than the centers (Schaetzl and Anderson, 2005; Troeh and Thompson, 2005). Sodic horizons in the solonization process may disconnect the soil pedon from groundwater because of the hydraulic gradient between the A and B horizons, preventing Na from moving into the A horizon by capillary rise (Miller and Brierley, 2011). The “biscuit top” can be found in sodic soils of North Dakota, but after many years of cultivation, the columnar structure of the B<sub>tn</sub> horizon is often mechanically degraded, and therefore the visual identification of this horizon is more difficult.

Solodization (dealkalization) occurs when Na in the B horizon is gradually leached from soil by precipitation and or irrigation, where Na slowly leaches from the B horizon and is replaced by divalent cations (Ca or Mg) (Schaetzl and Anderson, 2005). Some soils in the Canadian and North Dakota Prairies have the morphological properties of Solonetz soil but may not meet the chemical criteria established by the U.S. Salinity Laboratory because these soils have a different degree of solodization (Miller and Brierley, 2011; Seelig et al., 1990). Columns in the B<sub>tn</sub> horizon start to break down because of loss of Na, and cracks between columns are continually stripped by water, leaving white sand or silt and forming a “glossic” soil. Eventually, as leaching continues, Na is replaced by hydrogen (H) and the columns are completely degraded,

and replaced by prisms part to angular blocky structure. The upper soil becomes acidic, but the subsoil remains high in sodium with high pH, resulting in a soil called solod or soloth (Schaeztl and Anderson, 2005; White, 1967). Solodization more often occurs in humid areas or the lower landscape positions, and is inhibited in dry climates, which prevents leaching (Miller and Brierley, 2011).

### **Sodic Soil Distribution**

Sodic soils, as a major type of salt-affected soil, are distributed differently worldwide, and their areal extent is most prevalent in Australia, followed by North and Central Asia, and then South America (Szabolcs, 1979; Szabolcs, 1989). The estimated global area covered by salt-affected soils is about 930 million ha (2303 million acres), among which sodic soils occupy about 581 million ha (Sumner and Naidu, 1998; Szabolcs, 1989) (Table 1). However, global distribution is still increasing with deterioration of productive soils because of poor land management practices such as application of untreated saline ground water with high sodium adsorption ratio (SAR) for irrigation (Qadir and Oster, 2004). For example, land degradation caused by saline and sodic problems has increased in last few decades in China's Yellow River basin and the Aral Sea basin in Central Asia (Cai et al., 2003; Gupta and Abrol, 2000). Attempts to increase global food production should consider appropriate land management practices that minimize soil deterioration due to salt accumulation.

In North America, most sodic soils occur in the arid and semiarid climates of the Great Plains of Prairie provinces of central and western Canada and the Northern United States (FAO, 1991). Sodic soils occur in many areas of Northern Great Plains (as shown in Fig. 1), and in North Dakota, about 4.7 million acres (1.9 million ha) of sodium-affected soils exist within this region (J. Brennan, personal communication, NRCS North Dakota, 2008) (Table 2).

Table 1. Global distribution of salt affected soils (summarized from Szabolcs, 1979; Szabolcs, 1989).

Continent	Areas in millions of ha		
	Saline <sup>†</sup>	Sodic (Alkali) <sup>‡</sup>	Total
North America	6.2	9.6	15.8
Central America	2.0	—	2.0
South America	69.4	59.6	129.0
Africa	53.5	27.0	80.5
South Asia	83.3	1.8	85.1
North & Central Asia	91.6	120.1	211.7
Southeast Asia	20.0	—	20.0
Australasia	17.4	340.0	357.4
Europe	7.8	22.9	30.7
Total	351.5	581.0	932.2

<sup>†</sup> Saline is defined as presence of soluble salts in soil or water which may result in reduced plant production.

<sup>‡</sup> Sodic is defined as presence of high proportion of sodium ions relative to other cations in a soil or in a water, in the United States and throughout much of the rest of the world, the ESP value of greater than 15 was the criteria for separating sodic soils, while in Australasia, the ESP value was lowered to 6.

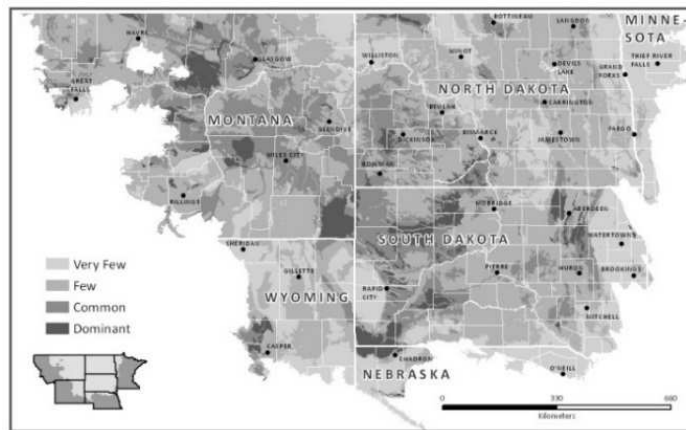


Fig. 1. Sodic soils with SAR values  $\geq 10$  within 75 cm of the surface in the Northern Great Plains. The classes in the map are: Very few (2% or less of the area impacted), Few (2-20% of the area impacted), Common (20-50% of the area impacted), and Dominant (more than 50% of the area impacted). Data were queried using SSURGO (Soil Survey Geographic Database) and analyzed using STATSGO (State Soil Geographic Database, USDA-NRCS, Washington, D.C.) (J. Brennan, personal communication, NRCS North Dakota, 2008).

Sodic soils in North Dakota are found in glacial landscapes underlain by marine deposits of cretaceous, shale and tertiary, but in western North Dakota are mainly associated with clayey

sediment of the Fort Union Formation in unglaciated regions (Kellogg, 1934; Sumner and Naidu, 1998). District microrelief on both glaciated and residual parent materials contribute to redistribution of precipitation (rain or snow), water and salt movement, therefore, resulting in different types of sodic soils (Seelig and Richardson, 1994).

Table 2. Saline and sodic soil area distributions (acres) within 75 cm of the surface in Northern Great Plains (NGP) states depending on soil EC value ( $\text{mmho cm}^{-1} = \text{dS m}^{-1}$ ) (J. Brennan, personal communication, NRCS North Dakota, 2008).

State	State acreage (NGP only)	Slight salinity (EC $\geq$ 4)	Moderate salinity (EC 8 -16)	Strong salinity (EC $\geq$ 16)	Saline acreage	Sodic SAR $\geq$ 10
-----acres-----						
Minnesota	6,137,839	18,765	28,881	2,054	49,700	40,000
Montana	50,748,014	5,759,776	4,232,391	816,309	10,808,476	9,650,000
Nebraska	6,159,382	21,220	113,805	5,350	140,376	400,000
North Dakota	45,341,198	2,216,638	3,434,435	146,810	5,797,884	4,730,000
South Dakota	45,972,193	3,686,677	4,245,279	551,347	8,483,303	7,920,000
Wyoming	15,839,425	417,162	613,408	26,889	1,057,459	990,000
Total	170,198,049	12,120,239	12,668,200	1,548,760	26,337,198	23,720,000

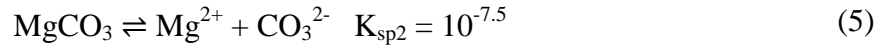
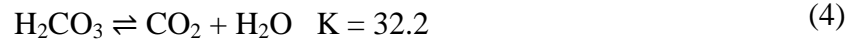
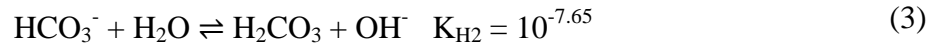
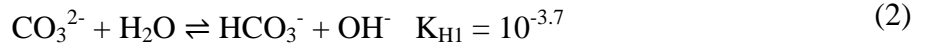
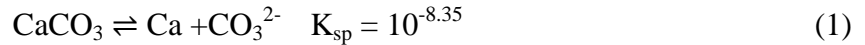
### Sodic Soils and the Processes Involved in Sodic Behavior

#### How were parameters for determining sodicity hazard established?

The U.S. classification of sodic soils is based on chemical properties and takes into consideration the minimum limits that affect crops. The pH of 8.5 was set as minimum limit for sodic soil classification by the U.S. Salinity Laboratory Staff in Riverside, California (U.S.



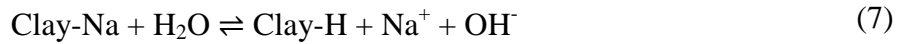
Salinity Laboratory Staff, 1954). Sodic soils lack appreciable amounts of soluble salts (associated with  $EC < 4 \text{ dS m}^{-1}$ ) but have appreciable amounts of less solubility salts capable of alkaline hydrolysis (e.g.  $\text{NaCO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ , and exchangeable Na on soil exchange sites). For example, in calcareous soils, calcite hydrolysis takes place in stepwise procedures of dissociation followed by subsequent hydrolysis and release of carbonate and bicarbonate ions according to Eq. (1 to 6) (Faure, 1998; Guerrero-Alves et al., 2002).



The balance of all charges in solution through the law of Mass Action and electrical neutrality at equilibrium during soil water reaction has been calculated from the concentration of each ion species and pH was estimated to be 8.36, which is responsible for the high pH of calcareous sodic soils (Faure, 1998). However, hydrolysis of  $\text{CaCO}_3$  or  $\text{MgCO}_3$  is limited due to their low solubility, and the major contribution to pH of a sodic soil results from dissociation and hydrolysis of appreciable quantities of  $\text{NaCO}_3$  and hydrolysis of exchangeable Na (Guerrero-Alves et al., 2002). This produces a higher pH (may be as high as 10) than other salts ( $\text{CaCO}_3$ ) (Abrol et al., 1988), but this high pH is not very common in soils of North Dakota even on sodic soils.

The rise of pH from hydrolysis of exchangeable Na in soil takes place according to Eq. (7 to 9) (Essington, 2004; Foster, 1954; Guerrero-Alves et al., 2002). In Eq. 7 exchangeable  $\text{Na}^+$  is

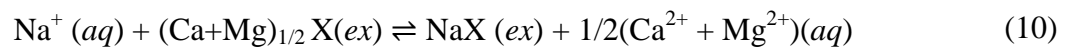
displaced by  $H^+$  in water, with  $Na^+$  and  $OH^-$  being released. Guerrero-Alves et al. (2002), however, demonstrated that the presence of “protonated clays” (HX) (X is clay) was not possible, and that the rise of pH of alkali sodic soils was probably attributed to the accumulation of alkaline Na salts. Guerrero-Alves et al. (2002) also proposed that the genesis of sodic soils were associated with soluble Na salts, which cause an increase of ESP and precipitation of  $CaCO_3$  and  $MgCO_3$  (Eq. 8 and 9). At ESP values between 10 and 60%, the  $NaHCO_3$  would accumulate and cause Ca and Mg to precipitate and relatively lower pH values would prevail, but when ESP was greater than 60%, pH could reach levels higher than 10. The pH values of 8.5 and greater almost always indicate an ESP of 15 or more by U.S. Salinity Laboratory Staff (1954).



Historically, soluble Na percentage was applied as an alkaline hazard to describe irrigation water with a high proportion of Na (U.S. Salinity Laboratory Staff, 1954). In 1921, Scofield and Headley (1921) investigated the effects of alkali water on a field and found that the cation constituents in irrigation water were related to the physical and chemical properties of soils. Furthermore, numerical studies conducted on 59 soil samples representing 12 irrigation districts in the western states of the USA broadly demonstrated the significant relationship between the soil solution Na percentage and ESP (U.S. Salinity Laboratory Staff, 1954).

The cation selectivity coefficient ( $K_G$ ) expressed by Gapon (1933) described and illustrated the impact of irrigation water on the sodicity of a soil. Saturation of the exchange complex and the concomitant displacement of divalent cations ( $Ca^{2+}$  or  $Mg^{2+}$ ) occurs by the reaction in Eq. (10), where the Gapon selectivity coefficient was expressed as in Eq. (11). In Eq

11, the ratio of  $[\text{NaX}]$  to  $[(\text{Ca}^{2+} + \text{Mg}^{2+})_{1/2} \text{X}]$  on the soil exchange complex was defined as exchangeable sodium ratio (ESR), and the ratio of the concentration of  $\text{Na}^+$  to divalent ions  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the soil solution (or irrigation water) was defined as SAR. Therefore,  $K_G$  was derived as  $K_G = \text{ESR}/\text{SAR}$  (Essington, 2004). The  $K_G$  value was derived by the U.S. Salinity Laboratory through the relationship between SAR and ESP as  $\text{ESP} = 100 (-0.0126 + 0.01475 * \text{SAR}) / (1 + ((-0.0126 + 0.01475 * \text{SAR})))$ , where the  $K_G$  was estimated to be about 0.015 in regression.



$$K_G = ([\text{NaX}] [\text{Ca}^{2+} + \text{Mg}^{2+}]^{1/2}) / ([(\text{Ca}^{2+} + \text{Mg}^{2+})_{1/2} \text{X}] [\text{Na}^+]) \quad (11)$$

Given the relationship between SAR and ESP though  $K_G$ , for convenience, it is reasonable to determine the SAR of the soil solution instead of making the complicated, time-consuming determination of ESP. The uses of soil solution SAR from saturated paste extracts overcome problems associated with the extraction of Na from the exchange site and estimation of CEC, especially in soils with appreciable soluble salts; therefore, the U.S. Salinity Laboratory Staff (1954) selected an SAR value of 13 to differentiate non-sodic from sodic soils instead of an  $\text{ESP} = 15$ . Unfortunately, the tap water used during hydraulic conductivity measurements had high concentrations of salts varying between 4 and 10  $\text{mmol}_c \text{L}^{-1}$  (0.4 to 1  $\text{dS m}^{-1}$ ), resulting in less hydraulic decay for the tested soils than those treated by distilled water or low salt-containing water (Shainberg et al., 1989). This situation probably contributes to the high SAR value in the USA sodic soil classification system. Some Australian studies using low salt-containing water for classifying sodic soils suggested lower values for classifying them and have defined sodic soils as having an ESP greater than or equal to 6 within the upper 1 m depth. The

Israeli soils also have a low SAR of 6-9 for sandy soils under irrigation during saturated conductivity reduction research (Sumner and Naidu, 1998).

### **Clay minerals**

The most common clay minerals in soils belong to the phyllosilicates (Schaetzl and Anderson, 2005). The phyllosilicates are composed of Si and Al and have sheet structures where for the Si sheet, three of the basal oxygens in each  $\text{SiO}_4$  tetrahedron share an oxygen with neighboring tetrahedrons, forming a pseudo-hexagon (Essington, 2004). In the Al sheets, the Al is coordinated to six hydroxyl groups and forms an octahedron (Klein and Dutrow, 2008). Phyllosilicate structures commonly include 1:1 and 2:1 ratios of Si:Al sheets. Apical oxygens in the Si tetrahedral layer are bonded to the OH group in the octahedron layer to join the two sheets together (Essington, 2004).

In the 1:1 types of clay, for example kaolinite, no isomorphic substitution results in a low net negative charge. Given this clay's small surface areas, it has a low CEC. The tightness of the t-t bond is a reason for the tight structure of kaolinite sheets. In the 2:1 clays the tetrahedron-octahedron-tetrahedron (t-o-t) layers are joined to each other by van der Waals bonds (Sumner and Naidu, 1998). Smectite is a group of 2:1 phyllosilicate minerals characterized by low layer charge of 0.2 to 0.6 moles per unit cell (Schaetzl and Anderson, 2005). Montmorillonite is a common smectite clay group commonly found in North Dakota (Franzen, 2013) and this clay has good cleavage in d-spacing and small size (Klein and Dutrow, 2008). The negative charge of montmorillonite is mainly derived from isomorphic substitution of  $\text{Al}^{3+}$  by  $\text{Mg}^{2+}$  in the octahedron sheet. The functional sites of montmorillonite arise from the octahedral sheet and are located in the siloxane cavity surface (Essington, 2004). This clay has a high reactivity with interlayer and adsorbed cations because this zone has high charge distribution over the 18 surface

oxygen atoms within the two interlayer surfaces (Essington, 2004). The forces by which interlayer cations are adsorbed to the montmorillonite surface is weaker than that in other types of clays (Grim, 1968; Schaetzl and Anderson, 2005). Charges derived from other types of clay occur mainly from the outer Si-tetrahedron substitution and result in a smaller distance between adjacent layers compared to montmorillonite (Schaetzl and Anderson, 2005). Only 20% of smectite's negative charges are derived from Si-tetrahedron substitution with the remaining 80% from isomorphic substitution in the octahedron; therefore, the bond between adjacent clay layers is weak resulting in water easily entering into the interlayers to hydrate cations (Grim, 1968). This result is consistent with what was found by Foster (1954) whereby the degree of swelling decreases with an increase in octahedral substitution in montmorillonite.

### **Cations and water associated with clay minerals**

When a surface functional group of clay reacts with ions in soil solution, a surface complex is formed and the negatively charged clay surface is neutralized by adsorbing cations and molecules in solution (Essington, 2004). Some ions reside on the is-plane (inner-sphere plane) of the mineral surface where there is no water molecule between the adsorbed ion and clay surface and are considered non-exchangeable, forming an is-plane exchange complex. Most of the exchangeable ions are held at the clay surface by electrostatic attraction on the os-plane (outer-sphere plane), where there is at least one water molecule between the adsorbed ion and clay surface functional group (Essington, 2004). The particle charge from the above two types of adsorbed ions together with the negative charge from clay, compose the net particle charge density of a clay mineral. The net particle charge ( $\sigma_p = \sigma_H + \sigma_{is} + \sigma_{os}$ ) must be balanced by the ion charge,  $\sigma_d$ , that resides in the diffuse ion swarm of the bulk solution, which is not bound to

the surface complex but is still associated with the surface, making soils electrically neutral (Essington, 2004).

The state of water in soils depends on its relationship to soil minerals, thus water can be found in pores, adsorbed on surfaces, and between interlayers of clay minerals (Hillel, 1998). The water molecule exists as a dipole molecule with two regions associated with hydroxyl bonds linked to protons and another two regions with lone pairs of electrons locating to the opposite side of the oxygen nucleus (Grim, 1968). The V- shape arrangement of the atomic nuclei of water results in the dipole effect of water and the net charge distribution of the water molecule resembles a tetrahedron (Faure, 1998). One water molecule is bound to another one at the opposite corners of the tetrahedron through hydrogen bonds, which are then joined to hexagonal groups and extended into a hexagonal sheet of water (Hendricks and Jefferson, 1938).

In each hexagonal group, one H of water is not involved in bonding within the water sheet and it is free to be coordinated to the surface of clay minerals by attraction between H and the surface oxygen layer of Si-tetrahedron in clay minerals (Grim, 1968). Water sheets occasionally are adsorbed to OH groups on the Al-octahedral layer of clay where the protons on OH groups are screened by excess electrons from the clay surface to make OH less electropositive. The first layer of water is bound to clay minerals by covalent bonds in an oriented direction and since the clay is negatively charged the positive end of water molecules is towards the clay surface with the negative end extending outward (Grim, 1968). When this occurs, the first layer of water bears another surface of negative charges which is available to absorb and build another layer of water molecules. Depending on the clay types (charge density and surface area), different layers of water molecules could be retained to clay minerals (Essington, 2004). Clay mineral surface layers are not exactly planar, having adsorbed cations on

them; therefore, the water sheets adsorbed to clay minerals may be distorted and a quasi-crystalline water sheet model is more likely (Klein and Dutrow, 2008).

### **Swelling**

Soil swelling is associated with the function of the interlayer region (Velde and Meunier, 2008), and the swelling property of soil clays is determined by the ability of interlayer cations to retain the water shell within this interlayer region. Interlayer cations, which remain close enough to the clay surface to balance the net total charge associated with the clay surface, are freely mobile and are able to be hydrated when soil is wetted; therefore, interlayer cations are responsible for holding water in clays (Essington, 2004). Hydration will occur if the potential energy of the water molecule is less in the hydration shell of the cation than it is in the hydrogen bond of the water sheet between the interlayer (Grim, 1968). The hydrated interlayer cations, with roughly spherical complexes, locate in clay surfaces to form the functional complex with clay (Velde and Meunier, 2008).

There are generally two factors controlling the functional complex: the size of the cation and its charge, both of which determine hydration energy (Sumner and Naidu, 1998). The capacity of cations to lose or conserve their water molecule shells is also related to the position of the interlayer cations located on the clay surface. When Na exists in the interlayer, it is located either near the position of negative charge, where the  $\text{Al}^{3+}$  cations replace  $\text{Si}^{4+}$ , or inside the ditrigonal cavity in the tetrahedral sheet (Velde and Meunier, 2008), therefore, the potential for  $\text{Na}^+$  to be hydrated is less than those cations outside of the cavity.

The  $\text{Ca}^{2+}$  ions have a very small hydration enthalpy so they remain strongly bonded to water molecules (Grim, 1968). The hydration radius of  $\text{Ca}^{2+}$  is about 12 Å, much greater than the ditrigonal cavity size (2.6 Å), so  $\text{Ca}^{2+}$  ions are located outside of the ditrigonal cavity. In sodic

soils high  $\text{Na}^+$  exists in solution, but unlike  $\text{Ca}^{2+}$ , the size of  $\text{Na}^+$  does not disrupt the water sheet structure adsorbed in the interlayer region. The water sheet is rigid enough that  $\text{Na}^+$  can neither diffuse through it nor shear it under stress, resulting in better maintenance of the water between interlayers (Grim, 1968; Velde and Meunier, 2008). On the other hand,  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  would disturb the water structure compared to  $\text{Na}^+$ . Sometimes, clay charge density also plays an important role in swelling (Grim, 1968).

With more water entering into the soil system and more membranes of water being adsorbed, the cation chemical potential in the interlayer and bulk solution becomes lower than that at the clay mineral surface (Essington, 2004). Therefore, cations on the particle surface and interlayer have a potential to diffuse into the adjacent bulk solution (lower chemical potential) by diffusive force (repulsive force) in order to reduce the enthalpy of the system (Engel and Reid, 2012). Original equilibrium between repulsive and attractive forces (known as van der Waals force) is broken due to a higher repulsive (diffusion) force, and the distance between adjacent interlayers of clay sheets begins to increase and the clay swells (Essington, 2004).

Water may be attracted to the clay surface by exchangeable cations, and the size of exchangeable cations and their tendency to be hydrated, influences the arrangement and orientation of water molecules on the clay surface (Grim, 1968). A high amount of Na stays in the siloxane ditrigonal cavity of the Si-sheet (with a size about  $2.8 \text{ \AA}$  (about  $0.26 \text{ nm}$ )) because the diameter of dehydrated Na is about  $1.96 \text{ \AA}$ . This fact allows an adequate fit of the  $\text{Na}^+$  ion in this position. In addition, negative charges on the siloxane functional sites diffuses over numerous surface oxygen atoms and has a higher base strength to dislodge the water of hydration around exchangeable Na compared to Ca (Essington, 2004). The above factors allow Na to retain relatively stable on the clay surface and the water of hydration of Na cannot easily escape from



the clay surface. This phenomenon was further demonstrated to be related with the disruptive effect of ions on the quasi-crystalline water sheet (hydration enthalpy -406 vs. -1577 kJ mol<sup>-1</sup> for Na<sup>+</sup> and Ca<sup>2+</sup>, respectively), indicating that water around Na is less tightly held than water around Ca, which results in minimal effect on disrupting the water-quasi-crystalline structure (Essington, 2004; Wang, 1954; Sumner and Naidu, 1998).

A Na-dominated smectite soil was found to have a thickness of three water molecule layers in the interlayer space. When the thickness of the clay double layer is beyond 7.5 Å, there is a gradual transition for Na into liquid water from the clay exchange site compared to the abrupt transition for Ca dominated soil (Grim, 1968). Page and Baver (1939) further demonstrated the difficulty for Na to be exchanged (tightly fixed to the clay surface) and diffused even though it is exposed to water where the percentage of replaceable Na ions fixed by drying is about 19% (16.2% for Ca, 54.5% for K, and 29% for Mg) indicating that the adverse effect of Na cannot be deleted completely by Ca. There is an initial rapid adsorption of water to the liquid limit (LL) when a dry soil is exposed to water, but there is usually a little more water adsorption when Na is high in soil (beyond the LL), which enhances swelling (Grim, 1968).

In explaining the interaction between a clay mineral species and cations, the Gouy-Chapman theory attributes the thickness of the diffuse-double layer (DDL) to both attractive and repulsive forces. Cations in the solution are pulled towards the soil surface by the attractive electrostatic force resulting in a higher concentration and corresponding high chemical potential in this zone while anions are inversely different (Essington, 2004). Therefore, cations on the particle surface have a potential to diffuse into the adjacent solution (repulsion force). The thickness of the DDL is described by the following equations (Eq. 12 to 14).

$$\sigma = (2EnkT)^{1/2}/\pi \sinh (ze\psi_0/2kT) \quad (12)$$

where,  $\sigma$  is the surface charge on particle;  $\psi_0$  is surface potential;  $n$  is electrolyte concentration in the solution;  $z$  is valence of countercharge;  $e$  is electronic charge;  $E$  is dielectric constant of solvent;  $k$  is Boltzmann's constant;  $T$  is temperature in K. Effective thickness of the diffuse double layer is obtained in Eq. (13) and (14) by Sumner and Naidu (1998) and Essington (2004)

$$1/k = (EkT/8 \pi z^2 e^2 n)^{1/2} \quad (13)$$

$$k^{-1} = 3.042(10^{-10}) / (Z I^{1/2}) \quad (14)$$

where  $Z$  is valence charge, and  $I$  is the ionic strength. When the soil solution is diluted by rainfall or irrigation, the divalent cations are leached by drainage,  $I$  is reduced, the thickness of the double layer begins to increase, interact and overlap, setting up a repulsive force on adjacent particles. When the repulsive force is greater than the attractive force a greater increase in thickness of the DDL occurs, initiating or increasing swelling (Essington, 2004).

### **Dispersion**

Soil swelling stops when the chemical potential between the interlayer and bulk solution is maintained and when the repulsion force (diffusion force) equals the attraction force (van der Waal force) (Sumner and Naidu, 1998). If this equilibration state is broken, dispersion may occur. Dispersion occurs on the basis of swelling if hydration continues and when hydration weakens the aggregate strength, and finally clays are dislodged from aggregates.

Dispersion is related with  $I$  of the soil solution whereby when the soluble salt concentration is less than a threshold concentration, defined by Quirk and Schofield (1955), there is decreased soil stability and water permeability with dispersed clay particles in the effluent solution (Panayiotopoulos et al., 2004; Zhang and Norton, 2002). The dispersed clay particles from aggregates in solution occurs because the distance between particles continually increases due to the low solution concentration (Eq. 14). When the distance on the adjacent smectite clay

particles is separated beyond 7 nm, they remain dispersed in suspension (Rengasamy and Sumer, 1998). Different soil clays have different basal spacing, so when a certain basal spacing value is passed, soil clay is separated from a swelling (volume expansion) into a dispersion phase. For example, in sodic soils, montmorillonite increases in c-axis spacing and when the spacing is greater than 40 Å the adjacent clay layers completely dissociate (Grim, 1968). During the dissociation process, large quasicrystals (QC) (i.e. domains) of soil clay are broken, Ca is retained in the interlayers of the QC and Na is retained on the external surface of broken QC, where Na on external surfaces forces the diffuse double layers apart (Pils et al., 2007). Finally, smaller QC of clay particles develop in solutions of low  $I$  while larger QC were not completely dissociated in high  $I$  (Pils et al., 2007).

### **Adverse Effects on Soils and Plants**

The disruptive effect of sodicity on soil structural stability is not only a function of the amount of Na (denoted by ESP and SAR values), but it is also strongly associated with the  $I$  of the soil solution (Essington, 2004). Dispersed clay particles can be demonstrated by the presence of clay films and/or an argillic horizon in the sodic soil profiles where the clay particles move with percolating water and migrate deeper into the soil profile (Miller and Brierley, 2011). The decrease of hydraulic properties (infiltration or hydraulic conductivity) together with dispersion, indicated by cloudy effluent or decrease of effluent transmittance, were explained by the fact that the electrolyte concentration of a leaching solution was not sufficient to balance the electrostatic repulsive force in soils (Ben-Hur et al., 2009). Dispersed particles were pronounced in clogging soil pores and swelling was pronounced in decreasing the volume of the inter-aggregate pores, resulting in inhibition of plant roots and water penetration (Ben-Hur et al., 2009; Sumer and Naidu, 1998). A minimum concentration value of soil solution was defined when the total

potential energy of the soil was zero and was called critical flocculation concentration (CFC). This is consistent with a definition of threshold electrolyte concentration (TEC) portrayed by Quirk and Schofield (1955) who found that no dispersion and significant decreases in permeability occurred at this TEC value in a sodic soil. Below the TEC, clay dispersion increased with successively decreasing electrolyte concentration under the same SAR (Panayiotopoulos et al., 2004). This phenomenon makes irrigation with saline water on sodic soils a possible approach in low precipitation regions (such as Israel) to remediate the sodic effect on soils and increase production yields (Sumner and Naidu, 1998).

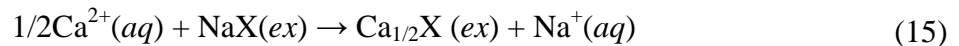
Sodic soils can increase surface water runoff, water ponding and crusting, all of which can be attributed to dispersion or swelling which may likely result in low seed germination, growth, and crop production (Sumner and Naidu, 1998). In some instances sodic soils may cause a wavy growth pattern due to these variables (Qadir et al., 2001; Sumer and Naidu, 1998). Increases in Na can also increase soil shear strength (Kyei-Baffour et al., 2004) because the plastic limit (PL) and liquid limit (LL) of sodic soils can result in decreased trafficability for walking and machinery (Earl, 1997).

Sodic soils influence plant growth not only through the adverse effects on the soil physical and chemical properties mentioned above, but also through the effect on soil microbial activities. Soil microbial biomass can linearly decrease with an increase of soil SAR, and therefore, biochemical processes essential for maintenance of soil quality can also decrease resulting in nutrient deficiencies for crop production (Rietz and Haynes, 2003). Root length density of wheat (*Triticum aestivum* cv. Amarok) was found to be decreased about 10 folds at the 40 cm depth of a sodic soil compared to the surface soil and resulted in a decreased yield (Gill et al., 2009). Choudhary et al (2011) reported that rice (*Oryza sativa*) yielded less than 1.5 Mg ha<sup>-1</sup>

for eight years in a sodic-water-irrigated field, 40% less than well-treated soils. Overall, the productivity indexes (PI) of sodic soils are generally very low, because of the poor structure and imbalance in plant available nutrients (Kellogg, 1934). For example, SAR may increase with depth of soil in many well-drained soils of North Dakota, but salts levels are in shallow horizons of sodic soils (“Leptic” subgroup taxonomy; salts are less than 40 cm depth) and cause concerns before tile drainage (Hopkins et al., 2012). For example, the Exline soil (Fine, smectitic, frigid Leptic Natrudolls) only has a PI of 30, but healthy soils such as the Arnegard soil (Fine-loamy, mixed, superactive, frigid Pachic Haplustolls) or Gardena (Coarse-silty, mixed, superactive, frigid Pachic Hapludolls) have a PI of 100 (NRCS Web Soil Survey).

### **Options for Sodic Soil Management**

Key strategies to improve sodic soil structure include reducing the SAR and ESP as well as maintaining an adequate “high” EC (Qadir et al., 2001). The reduction of ESP is a result of cation exchange, which occurs by displacement of the Na by Ca (Chen and Dick, 2011). This displacement process can be described by the Ca-NaX exchange reaction

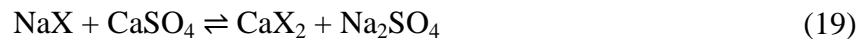
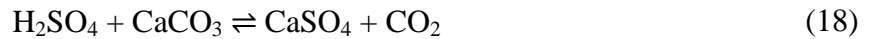


Incorporation of Ca amendments or potential release of Ca through chemical reaction in soil are beneficial in cation exchange. Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is one of the most popular amendments in agriculture to directly supply Ca (Chen and Dick, 2011) for sodic soil remediation. Gypsum dissociation releases Ca and  $\text{SO}_4$  which allows  $\text{Ca}^{2+}$  to replace  $\text{Na}^{+}$  (Eq. 15), which is accompanied by an increase in EC (greater than  $2.3 \text{ dS m}^{-1}$  at saturation) (Sumner and Naidu, 1998). Additional benefits of gypsum to soil include increased oxygen diffusion, root penetration, aggregate stability, and water infiltration (Chen and Dick, 2011). For example,

gypsum application resulted in the increased availability of O<sub>2</sub> and root penetration, which contributed to a 300% increase in grape production (Wheaton et al., 2002).

Historically, the application rate of gypsum to remediate sodic soils has varied with climate, sodic soil severity, and depth of sodic horizon (Sumer and Naidu, 1998). In order to calculate the gypsum application rate, critical factors include soil cation exchange capacity (CEC), original and a final desired ESP, soil exchangeable Na needed to be replaced (meq 100 g<sup>-1</sup>), and the depth of soil. The calculation process, which can be found in Appendix A, has four steps: Step 1) determine the Na to be replaced; Step 2) determine the amount of Ca required to replace the total charge of Na; Step 3) determine the amount of gypsum that can provide the above amount of Ca; and Step 4) the amount of gypsum should be converted to proper units and for the desired depth of incorporation (U.S. Salinity Laboratory Staff, 1954).

Other Ca-yielding sources include S, lime sulfur, FeS<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, FeSO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, or Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (Sumner and Naidu, 1998). These amendments provide Ca<sup>2+</sup> indirectly through calcite dissolution via acid or acid-forming materials (Choudhary et al., 2011; Sumner and Naidu, 1998). For example, S needs to be oxidized by soil microorganisms and therefore it is classified as a slow-acting amendment compared to gypsum through reaction in Eq. 16 to 19 (U.S. Salinity Laboratory Staff, 1954).



To remove the Na replaced by Ca, drainage strategies should be applied (Choudhary et al., 2011; Essington, 2004). Subsurface tile drainage installation in North Dakota has increased

in recent years with the objectives of reducing root-zone soil water and reducing salinity. Some soils that are being drained, however, are classified as either sodic or potentially sodic (Cihacek et al., 2012). Given the previously mentioned conditions that cause swelling and dispersion, loss of EC with drainage waters will likely increase drainage problems. Personal communications with farmers and visual observations have indicated that after tile drainage sodic areas do not drain as well as non-sodic-surrounding soils. For example, in a case study of Nahon sodic soils (Fine, smectitic, frigid Calcic Natrudolls) in North Dakota, salts were found to be accumulated on shallow soil profiles than deeper depth in wet cycles, which accompanied with SAR may affect hydraulic conductivity of water in tile drainage (Hopkins et al., 2012). This situation may have been caused by drainage of soluble salts thus reducing EC and initiation dispersion or that water movement through these sodic soils was always been less than adjacent non sodic soils and now this lack of drainage is much more visible compared to drainage of non sodic soils.

Determining where to apply amendments is problematic because sodic soils often display spatial variability at the field scale (Shouse et al., 2010). This variability results from the interaction of soil heterogeneity, microtopography, water flow patterns, and human management practices (Hopkins et al., 1991; Shouse et al., 2010). Non-homogeneity of sodicity is deemed one of the most striking factors for utilization and management of sodic soils (Yang et al., 2011). It is important to consider site-specific management of sodic soils, especially when considering economic variables including what amendment to use and how much investment should be applied on these low PI soils. For example, the cost of gypsum is about \$218 Mg<sup>-1</sup> (240 \$ /ton) (A. Hoiberg, personal communication, 2014) and given that two to seven Mg per ha may be needed, the cost of gypsum alone may be prohibitory to many landowners. Determining where sodic soils are located and their depth within the soil profile will optimize site-specific

application of amendments and allow land managers to determine economic viability of land improvement.

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# **PAPER 1. THE RELATIONSHIP BETWEEN SAR<sub>1:5</sub> AND SARE OF THREE EXTRACTION METHODS**

## **Abstract**

Cations extracted from soil using non-standard techniques are used to calculate the sodium adsorption ratio (SAR). To interpret these values, analytical approaches for converting alternative approaches to standard approaches are needed. The objectives of this research were to develop the relationship between the standard approach (SARE) and alternative approaches where the cations were in 1 to 5 soil/water ratios and were mixed by shaking, stirring, and a USDA-NRCS method (or allowed to reach equilibrium). One hundred soils sampled from glacial parent materials in North Dakota, USA, were selected for this study. The SAR values from the four methods were highly correlated to each other. Based on strength of fit, skewness, and normality of residuals the shaking approach produced the best results using simple linear regression. Outliers of the three models (simple linear regression, robust regression and Model 2) had high calcite concentrations. In addition, the relationship between Ca in 1:5 and saturated paste extracts showed poor relationships, indicating that Ca had an influence on the relationship between SAR<sub>1:5</sub> and SARE. Therefore, the soil data were classified into calcareous and non-calcareous and allowed for better model predictions. Therefore, to predict a SARE of soils from 1:5 data, it is recommended that the soil-calcite concentration be considered.

Keywords: Sodium adsorption ratio (SAR); SAR<sub>1:5</sub>; SARE; Equilibration methods; Calcareous soils.

## **Introduction**

Traditionally US sodic soils have E<sub>c</sub>e values < 4 dS m<sup>-1</sup>, exchangeable sodium percentage (ESP) ≥ 15, saturated paste extract sodium adsorption ratio (SARE) ≥ 13, and pH >

8.5 (NRCS, 2004; U.S. Soil Salinity Laboratory Staff, 1954). This convention is based on the ratio between the relative amount of sodium on the exchange site (ESP) or in the soil solution (SAR). The Gapon equation empirically describes the relationship between ESP and SAR (Essington, 2004). Both ESP and SAR are widely-used parameters to evaluate the impact of sodium on soil behavior. The SAR is a quicker and simpler measurement than ESP particularly in diluted soil to water ratios than a saturated paste extracts (Chi and Wang, 2010; U.S. Soil Salinity Laboratory Staff, 1954). The chemical expression of SAR is Eq. 20:

$$\text{SAR} = \text{Na}^+ / [(\text{Ca}^{2+} + \text{Mg}^{2+})/2]^{1/2} \quad (20)$$

where cation units are  $\text{mmol}_c \text{L}^{-1}$ . To determine the  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  concentrations in soil solution in Eq. (20), a number of extraction methods have been used (Faulkner et al., 2001) which include various dilution ratios. For example, the U.S. Soil Salinity Laboratory Staff (1954) determined cation concentrations from vacuum-filtered extracts from saturated pastes, Cammerat (1991) measured cation concentrations from 1:1 soil to water extracts, Ternan et al. (1998) used 1:2 soil to water extracts, and Chi and Wang (2010) determined SAR from both saturated pastes and 1:5 soil to water extracts.

The saturated paste of soil is a widely used extraction method that is recognized as a conventional standard, however, the process of making saturation paste extracts can be time consuming and difficulties have been encountered in determination of the proper soil saturation point (Longenecker and Lyerly, 1964; U.S. Soil Salinity Laboratory Staff, 1954). Among the diluted ratios mentioned above, the 1:5 ratio is the preferred method for determining soil properties in Australia and China (Rayment and Lyons, 2011). The 1:5 ratio dissolves larger amounts of solutes than the saturation paste extract, especially for sparingly soluble salts (Reitemeier, 1946). The 1:5 extract ( $\text{SAR}_{1:5}$ ) is a convenient alternative method to saturated paste



extracts. Even though the 1:5 ratio is comparatively easy and repeatable, the soil-solution equilibration process has varied from mechanical shaking to stirring, with and without subsequent filtration (Chi and Wang, 2010; Rayment and Higginson, 1992; U.S. Soil Salinity Laboratory Staff, 1954), which may result in corresponding changes in SAR<sub>1:5</sub>.

The relationships between SAR<sub>e</sub> and SAR<sub>1:5</sub> is dependent on soil texture (Chi and Wang, 2010). This relationship was attributed to Ca, Mg, and Na concentrations in the saturated paste extracts being correlated to those in 1:5 extracts (Somnez et al., 2008), and there is a strong relationship between Na and the sum of Ca and Mg extracted from both saturated and 1:5 extracts (Ozcan et al., 2006). Rengasamy et al. (1984) reported that SAR values calculated for the 1:5 and saturated paste techniques for Australian red-brown earth topsoils (Alfisols) were almost identical. The relationship, however, has not been consistent among studies (Chi and Wang, 2010; Rengasamy et al., 1984). Our research objective was to elucidate the relationship between SAR<sub>1:5</sub> and SAR<sub>e</sub> under three different mixing methods (shaking, stirring, and a 1:5 USDA-NRCS equilibration) and also determine the effect of calcite on these relationships.

## **Materials and Methods**

### **Soil samples**

Soil samples used in this study (n = 100) were from Benson and Ramsey counties in North Dakota, USA (approximately lat. 48°11'34"– 48°33'36" N, long. 98°59'33"– 99°41'53" W), which lie in the Northern Great Plains. Samples were collected from three depths 0–15, 15–30, and 30–60 cm in 2009. All soils are Mollisols that varied from medium to fine in texture (He et al., 2013). Saturated paste extracts were prepared following the methods outlined by the U.S. Salinity Laboratory Staff (1954), Na, Ca, and Mg were determined using an atomic absorption spectrophotometer (Model 200A; Buck Scientific), and SAR<sub>e</sub> was determined using Eq. (20).

Due to small sample quantities from year 2009, 66 samples from the same locations and depths from a 2005 sampling were used to determine calcite and gypsum content. Given the relative stability of these secondary minerals, low annual precipitation between 26 and 54 cm since 2005 (excluding snowfall) accompanied by high evaporation (NDAWN stations: Devils lake Muni AP, ND at 48.12° N, 98.90°W, 439.2 m elevation; Devils lake Kdlr, ND at 48.11° N, 98.87°W, 446.2 m elevation) and no irrigation in the area, the gypsum and calcite content would not have appreciably changed within three years. Gypsum content was determined using water dissolution followed by acetone precipitation and EC measurement in subsequent water dissolution (Soil Survey Staff 2004, method 4E2a). Calcite content was determined by determining the pressure of soil reaction with acid based on the standard curve from specific amounts of pure CaCO<sub>3</sub> and the corresponding pressure reading (Williams, 1949).

### **Shaking, stirring, and USDA-NRCS (2011) equilibration mixing**

Three alternative methods of mixing 1:5 soil to solutions ratios (7 g soil: 35 mL of deionized water) were compared with the traditional saturation extract. The methods were: 1, shaking, 2, stirring, and 3, an updated USDA-NRCS (2011) 1:5 equilibration method. The shaking method involved reciprocal shaking for 8 h; the stirring method employed glass rod stirring 10s every 2 h over an 8 h period, and the equilibration (USDA-NRCS, 2011) method samples were maintained at room temperature for 23 h prior to agitation by a mechanical shaker for 1 h. Final supernatants from each sample of each equilibration method were obtained by filtering through #2 Whatman filter paper (Cat. No. 1002-110) and then through a syringe filter (Cat. 28143-272, VWR) into plastic vials. Cation concentrations were determined using inductively coupled plasma spectrometry by the National Soil Survey Center in Lincoln, NE USA. The SAR<sub>1:5</sub> was calculated using Eq. (20).

## **Statistical analysis**

Pearson correlation coefficients and zero order models between the extraction techniques were calculated in SAS 9.3 (SAS Inc., Cary, NC). Hat Diagonal and DFBETAS were calculated in SAS to check the presence of outliers and influential data during regression. The hat diagonal (H) is calculated by  $2p/n$  and data greater than H indicates influential data, where p is the number of parameters ( $p = 2$  in our study, the intercept and slope), and n is the sample size (100). The DFBETAS was calculated as  $2/\sqrt{n}$ , and results greater than  $2/\sqrt{n}$  were outliers. Residuals percent change in normal and kernel shape, and residual distribution with quartile were checked for normality. The relationship between measured SARE and SARE values estimated from the SAR<sub>1:5</sub> vs SARE regression models (model 1 obtained from calcareous or non-calcareous soils) were also determined.

## **Results and Discussion**

### **Correlation of SAR<sub>1:5</sub> values among three equilibration methods**

Each equilibration method produced different values for the same soil sample; companion studies (He et al., 2012; He et al., 2013) yielded similar relationship between EC<sub>1:5</sub> values for the same soil samples. Although the SAR<sub>1:5</sub> values were different from one another, Pearson correlation coefficients ( $r$ ) were all significant ( $P < 0.001$ ), indicating that SAR<sub>1:5</sub> values from one method could be used to predict results from another equilibration method (Table 3), which was again similar to the results in the He et al. (2013) EC<sub>1:5</sub> study.

Table 3. Pearson correlation coefficients between SAR<sub>1:5</sub> values from 3 different 1:5 equilibration methods (shaking, stirring, and USDA-NRCS equilibration) and saturated paste extract SARE.

	Parameters	SAR <sub>1:5</sub> shaking	SAR <sub>1:5</sub> stirring	SAR <sub>1:5</sub> USDA-NRCS	SARE
SAR <sub>1:5</sub> shaking	<i>r</i>	1.00	0.98	0.94	0.53
	<i>P</i>	-	< 0.001	< 0.001	< 0.001
SAR <sub>1:5</sub> stirring	<i>r</i>	0.98	1.00	0.94	0.61
	<i>P</i>	< 0.001	-	< 0.001	< 0.001
SAR <sub>1:5</sub> USDA-NRCS	<i>r</i>	0.94	0.94	1.00	0.52
	<i>P</i>	< 0.001	< 0.001	-	< 0.001
SARE	<i>r</i>	0.53	0.61	0.52	1.00
	<i>P</i>	< 0.001	< 0.001	< 0.001	-

### Relationship between SAR<sub>1:5</sub> and SARE

The relationship between SAR<sub>1:5</sub> and SARE was established using Model 1 (simple linear regression), robust regression, and Model 2. The results for three models across the three equilibration methods were validated by comparing different important inferences associated with the regression analysis (Mendenhall and Sincich, 2003). The relationships for all three models were significant, the Model 1 and robust regression were similar in the parameter estimates (slope and intercept) but Model 2 was different for all three equilibration methods (see Fig. 2, stirring method for example). In the parameter estimates (Fig. 2), the slope and intercept for model 1 were 1.79 and 3.08, respectively, and for robust model were 1.91 and 2.74, but for model 2 were 4.29 and -2.31. SAR<sub>1:5</sub> and SARE were analyzed separately and they were found to be normally distributed. The residual distribution showed a normal bell-shape and residuals vs SAR<sub>1:5</sub> also indicted a normal distribution for model 1 and robust regression. Model 2 showed left skewness in residual distribution with percent and had a poor scattering of residuals vs SAR<sub>1:5</sub>. Therefore, even though the relationship between SAR<sub>1:5</sub> and SARE in Model 2 covers most of data through the regression compared to the other two models as shown in Fig. 2, model

2 was not reasonable due to the high scattering in residuals. In addition, the  $r^2$  in Model 2 was not increased compared to the other two models. Based on all the statistical results above, Model 1 or robust regression were selected for the relationship between SAR<sub>1:5</sub> and SARE.

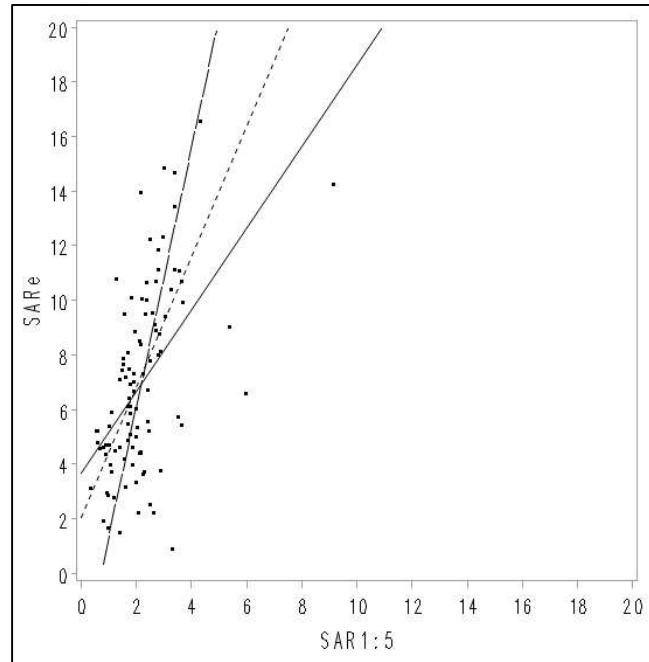


Fig. 2. Relationships between sodium adsorption ratio of 1:5 soil/water extract (SAR<sub>1:5</sub>) and saturated paste extract (SARE) for 100 samples for stirring method established using model 1 (solid line), robust regression (short-dashed line), and model 2 (long-dashed line).

The  $r^2$  for SAR<sub>1:5</sub> associated with SARE in simple linear regression model 1 was low, with 0.29, 0.37, and 0.27 for shaking, stirring, and NRCS equilibration method, respectively. The linear regression lines were strongly influenced by outliers (Fig. 2). These findings differed from previous work where, for Australian soils, SAR<sub>1:5</sub> was approximately equal to SARE (Rengasamy et al., 1984), and in Chinese soils where there was a strong relationship ( $r^2 > 0.9$ ) between SAR<sub>1:5</sub> and SARE (Chi and Wang, 2010).

Outliers were observed for the relationships between SAR<sub>1:5</sub> and SARE for three models across three methods. For example, in stirring method, the intercept of DFBETAS, one of the

indexes to determine outliers, ranged from -0.25 to 0.86 with 4 of soils greater than 0.2, indicating that these four soils were outliers. In addition, Hat matrix, COVRATIO, and DFFITS determination also identified more outliers. In our study, it was found that most of the outliers were high calcareous soils. Therefore, it is reasonable to divide the soils into calcareous (>4% calcite) and non-calcareous (<4% calcite) and determine the relationship between SAR<sub>1.5</sub> and SARE separately. Calcite was not determined in the study of Chi and Wang (2010), however, who made an assumption that calcite dissolution had an influence on the relationships between cation concentrations in both extracts. The content of calcite distribution in soils of Songnen Plain China ranges from 47 to 97.2 g kg<sup>-1</sup> (Wang, 1993), which indicated a lack of consideration of calcite effect in Chi and Wang's study. In addition, no calcite was detected in the Red-brown earth soils and no outliers were mentioned in the study of Rengasamy et al. (1984), which was beneficial for providing an accurate and significant relationships between SAR<sub>1.5</sub> and total cation concentration (TCC) (TCC= 1.46SAR+1.44) to determine soil dispersion and flocculation.

The strength of the relationship between SAR<sub>1.5</sub> and SARE was improved and was still significant when the soils were classified as calcareous and non-calcareous. For calcareous soils, the  $r^2$  was increased to 0.47, 0.48, and 0.49 for shaking, stirring, and NRCS equilibration method, respectively (Fig. 3, Table 4). Residuals were all normally distributed, and the presence of outliers was also greatly decreased. However, for non-calcareous soils, the relationship between SAR<sub>1.5</sub> and SARE was not increased and  $r^2$  was similar to that in the original dataset. The influential data with very high and low SAR values pulled down the regression (low  $r^2$ ). Therefore, presence of calcite must be considered when establishing the relationship of SAR. The effect of calcite was probably related with the slow Ca dissolution due to low solubility (DeSutter, 2008), which influenced the SAR calculation. Many studies have also shown the

calcite effect on the relationship between SAR<sub>1:5</sub> and SARE, where calcite behaved as a cement bridging across soil particles, influenced soil structure, and therefore, affected the ability of soluble salts to dissolve (Cheng et al., 2013; Keren and Ben-Hur, 2003).

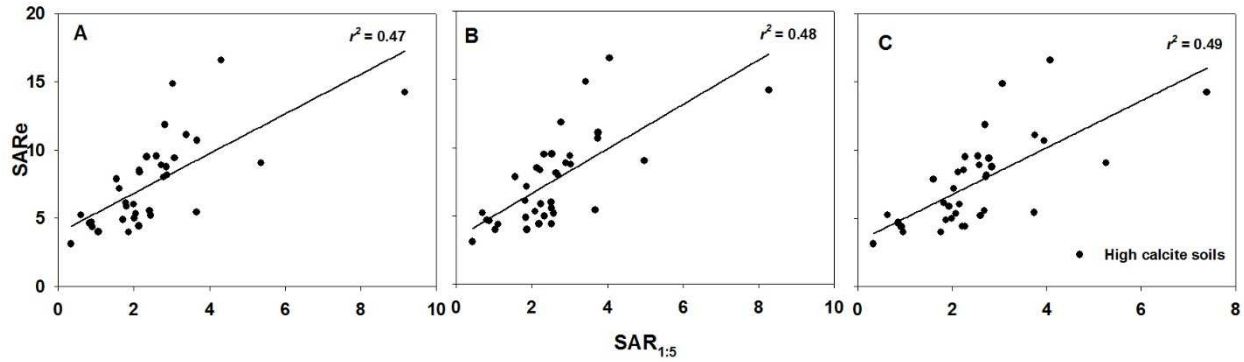


Fig. 3. Relationships between sodium adsorption ratio of 1:5 soil/water extract (SAR<sub>1:5</sub>) and saturated paste extract (SARE) for calcareous soil samples for three extraction methods: A (shaking), B (stirring), and C (USDA-NRCS equilibration).

### Cation relationships

Several studies (Chi and Wang, 2010; Sonmez et al., 2008) attributed the weak relationship between SARE and SAR<sub>1:5</sub> to different cation concentrations between the two extracts. Chi and Wang (2010) found that SARE cannot be reliably determined from 1:5 extracts, although Na concentration in saturated paste extracts was highly related with Na<sub>1:5</sub>. In this study, regression equations describing the relationships for Na concentration (Na<sub>SP</sub> vs Na<sub>1:5</sub>) and for Mg concentration (Mg<sub>SP</sub> vs Mg<sub>1:5</sub>) across each equilibration method were linear and highly correlated (Table 5). Sonmez et al. (2008) found similar significant linear relationships for these cations. The Ca concentration from saturated paste extracts in our study, however, was not strongly linearly related with the Ca<sub>1:5</sub> with  $r^2$  lower than 0.34 (Table 5). This differs from the results of Sonmez et al. (2008), which yielded a stronger linear relationship between Ca<sub>SP</sub> vs. Ca<sub>1:5</sub> with  $r^2$  of 0.83.

Table 4. Relationships between SAR<sub>1:5</sub> and SARE for calcareous and non-calcareous soils conducted by A (shaking), B (stirring), and C (USDA-NRCS equilibration) using model 1.

Extraction methods	Regression equation	RMSE <sup>†</sup>	r <sup>2</sup>
Calcareous			
A	$y^{\ddagger} = 1.45x^{\S} + 3.92$	2.42	0.47
B	$y = 1.63x + 3.39$	2.39	0.48
C	$y = 1.72x + 3.30$	2.38	0.49
Non-calcareous			
A	$y = 1.59x + 3.42$	2.99	0.20
B	$y = 2.03x + 2.67$	2.74	0.33
C	$y = 1.46x + 3.67$	2.94	0.23

<sup>†</sup> RMSE, Root mean square error.

<sup>‡</sup> y, SARE value.

<sup>§</sup> x, SAR<sub>1:5</sub> value.

Table 5. Coefficients of determination (r<sup>2</sup>) and regression equations describing the relationships of respective cation concentration between 1:5 and saturated paste extracts across (A) shaking, (B) stirring, and (C) USDA-NRCS equilibrations.

Cation type	Method	Regression equation	r <sup>2</sup>	P
mmol(c) L <sup>-1</sup>				
Na	A	$Na_{SP}^{\ddagger} = 7.02(Na_{1:5}^{\ddagger}) + 7.07$	0.76	< 0.0001
	B	$Na_{SP} = 7.43(Na_{1:5}) + 7.04$	0.78	< 0.0001
	C	$Na_{SP} = 6.90(Na_{1:5}) + 6.97$	0.78	< 0.0001
Mg	A	$Mg_{SP} = 5.83(Mg_{1:5}) + 14.6$	0.68	< 0.0001
	B	$Mg_{SP} = 6.50(Mg_{1:5}) + 13.3$	0.68	< 0.0001
	C	$Mg_{SP} = 5.56(Mg_{1:5}) + 14.6$	0.68	< 0.0001
Ca	A	$Ca_{SP} = 0.48(Ca_{1:5}) + 17.3$	0.23	< 0.0001
	B	$Ca_{SP} = 0.94(Ca_{1:5}) + 15.5$	0.34	< 0.0001
	C	$Ca_{SP} = 0.50(Ca_{1:5}) + 17.2$	0.22	< 0.0001

<sup>†</sup> SP, saturated paste extracts.

<sup>‡</sup> 1:5, 1:5 soil to water extracts.

The variation in Ca concentrations and poor relationship for Ca between Ca<sub>SP</sub> and Ca<sub>1:5</sub> shown in Table 5 was thought to be related with the presence of sparingly soluble salts, i.e. gypsum and calcite, which dissolve more completely at the higher water content of the 1:5 than the saturated paste extracts, thus increasing Ca contribution to the solution phase (Visconti et al., 2010). The non-proportionality relationship between Ca concentration in 1:5 and saturated paste



extracts reduced the strength of the calculated relationship between SAR<sub>e</sub> and SAR<sub>1:5</sub>. The EC<sub>1:5</sub> was lower in the 1:5 extracts than saturated paste extracts a higher soil E<sub>c</sub> for the same soil (He et al., 2013), and therefore, the ionic strength in the dilution of the 1:5 ratio was weaker than saturated paste. The reaction from calcite dissolution resulting in higher Ca and CO<sub>3</sub> and the concentration could be enhanced in 1:5 extracts because of the lower EC<sub>1:5</sub> and its effect on the solubility of CaCO<sub>3</sub> (Faure, 1998). This is because the lower EC (ionic strength) for the 1:5 ratio extracts increased calcite dissolution according to the equilibrium constant theory (Faure, 1998). Higher Ca concentration from calcite dissolution would probably affect the Na/Ca relationship in the 1:5 and saturation paste extracts. The poor Ca<sub>SP</sub> and Ca<sub>1:5</sub> relationship influenced the expression of SAR and therefore the relationship between SAR<sub>1:5</sub> and SAR<sub>e</sub>, even though Na and Mg behave in a strongly linear relationship for the two methods. The presence of outliers in the regression analysis further indicates the influence of calcites.

In our soils, calcite was detected in both surface and subsurface horizons which ranged from 0.3 to 31% and about half of the samples had more than 3% by mass. The presence of calcite was consistent with the “calcareous reaction class” as defined by Soil Taxonomy for soils in our study. Gypsum occurred only in 21% of the soil samples and ranged from 1 to 23%. Most samples that contained gypsum had between 1 and 5% and the geometric mean mass was 2.6%. Low solubility of gypsum (1.9 g L<sup>-1</sup>) and calcite (0.06 g L<sup>-1</sup> in 0.00032 atm of CO<sub>2</sub>) at 20 °C (FAO, 1973) likely change the Ca concentration and are responsible for the poor relationship of Ca between the SAR<sub>e</sub> and SAR<sub>1:5</sub> extracts. Low concentrations of calcite in the Sonmez et al. (2008) soils is confirmed by the pH values being less than 7, which may account for their strong linear relationships between saturated paste and 1:5 extracts, which is different from the regression results in our study.

## Measured SARE and predicted SARE values from model with calcareous soils

Due to the low value of  $r^2$  for all three methods, the regression line established for the entire set data needs to be used with caution when making estimations. The regression established for calcareous soils can be used for prediction. The regression line was established between measured SARE and predicted SARE and most of the data fell close to the regression and the 1:1 line (Fig. 4). The soils with high SAR in our study generally had high ECe and ionic strength (He et al., 2013), and therefore, Ca dissolution is slow in a saturated solution environment. But in the 1:5 ratio water, more dilution occurred compared to the saturated state, the ionic strength was lower and was beneficial for dissolution of more Ca, therefore, the SAR<sub>1:5</sub> value was affected which resulted in change in prediction of SARE from the SAR<sub>1:5</sub>. Comparison of the measured soil SARE and that estimated from the regression model indicated that regression was convenient if the soils are calcareous soils. For non-calcareous soils, the regression relationship between SAR<sub>1:5</sub> and SARE had a very low  $r^2$ , around 0.20. Therefore, SARE cannot be adequately estimated from SAR<sub>1:5</sub> for non-calcareous soils.

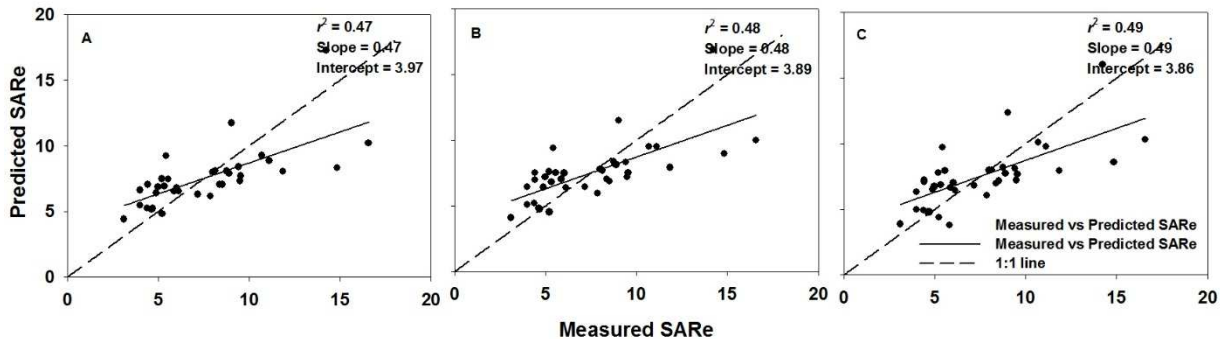


Fig. 4. Regression relationship between measured sodium adsorption ratio of saturated paste extract (SARE) and estimated SARE from models with calcareous soils for three extraction methods: A (shaking), B (stirring), and C (USDA-NRCS equilibration).

In order to further validate the models, the measured SARE and the values that were estimated by regression models in Fig. 3 for calcareous soils were compared and the root mean

square errors were determined. Root mean square error was 0.47, 0.48, and 0.49 for shaking, stirring, and NRCS method, separately, indicating that the model in Fig. 3 is acceptable for predicting SARE from SAR<sub>1:5</sub>. The measured SARE values were further validated against the SARE values that were estimated by regression equations of Chi and Wang (2010). The calculated mean SARE values for shaking, stirring, and USDA-NRCS (2011) were 32.6, 33.3, and 32.4 using the average regression equation in Chi and Wang (2010) ( $SARE = 13.19 \times SAR_{1:5}$ ), while the predicted SARE values through the model of our study were 5.13, 5.10, and 5.06, respectively. The SARE values between our model and that in Chi and Wang (2010) differed by about 84% (values in our study were lower) for the three equilibration methods.

### **Conclusions**

The SAR values determined from 1:5 soil to water extracts were correlated among three different equilibration methods (shaking, stirring, and NRCS equilibration). The simple linear regression and robust regression worked better than model 2 for establishing the relationship between SAR<sub>1:5</sub> and SARE. The predicted model for calcareous soils could adequately predict SARE from SAR<sub>1:5</sub> compared to non-calcareous soils. Caution should be taken when comparing SAR data from different studies or predicting SARE from SAR<sub>1:5</sub> data unless the same soil to water ratio or equilibration method is used. Lastly, the results of this study of glacial drift soils in North Dakota should be applicable to many soils of the Great Plains which have similar characteristics (carbonates, gypsum, and Na).

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## **PAPER 2. DISPERSION OF PURE CLAY MINERALS AS INFLUENCED BY CALCIUM/MAGNESIUM RATIOS, SODIUM ADSORPTION RATIO, AND ELECTRICAL CONDUCTIVITY**

### **Abstract**

Sodium concentration and the soil solutions Ca and Mg ratio may influence soil dispersion, and water movement. This study investigated the impact of electrical conductivity (EC), sodium adsorption ratio (SAR), and Ca/Mg ratios on dispersion thresholds of pure clay minerals (montmorillonite, illite, and kaolinite). Replicated laboratory studies were conducted where the impact of SAR (1, 5, 12, or 24), EC (0.5 –16 dS m<sup>-1</sup>), and specific Ca/Mg ratios on clay dispersion was determined. The results showed that Ca/Mg ratios did not influence clay dispersion of montmorillonite and kaolinite. For illite at a SAR of 12, however, dispersion was reduced by reducing the Ca/Mg ratio from 1/0, 2/1, and 1/2 to 0/1. Dispersion thresholds were < 6 dS m<sup>-1</sup> across all clays. At a SAR of 12, dispersion occurred for EC < 2 dS m<sup>-1</sup>. Kaolinite exhibited little, if any, dispersion. These results indicate that in soils having little or no organic carbon (i.e. subsoils), Mg does not influence dispersion thresholds and that dispersion risks can be reduced by adopting practices that maintain the EC >2 dS m<sup>-1</sup>.

### **Introduction**

Soil swelling and dispersion can result in the reduction of water infiltration and subsequent increase in water runoff and soil erosion (Sumner and Naidu, 1998). Factors that influence the degree of swelling and dispersion are the concentration of Na on soil exchange sites, clay mineralogy, the presence of cementing agents, and the ionic strength of the soil solution, which is commonly reported as electrical conductivity (EC) (Zhang and Norton, 2002). The saturated hydraulic conductivity (*K*<sub>sat</sub>), along with the quantification of clay and silt

concentrations in the effluent, have been used to effectively assess swelling and dispersion, which have then been related to relationships between exchangeable Na percentage (ESP), SAR, and EC (Sumner and Naidu, 1998; Zhang and Norton, 2002). These types of experiments have allowed increased understanding of threshold electrolyte concentrations at certain ESP values (Quirk and Schofield, 1955) and critical flocculation concentrations of soils with different SARs (Panayiotopoulos et al., 2004).

The U.S. Salinity Laboratory Staff (1954) grouped Mg and Ca together as having similar beneficial effects on structural stability, and this suggestion was substantiated by Rahman and Rowell (1979) and Yousaf et al. (1987). Studies have shown, however, that Mg-dominated soils accumulated greater exchangeable Na than did Ca-dominated soils (Vukadinovic and Rengel, 2007) and that the concentration of dispersed clay in a Catlin soil (Fine-silty, mixed, mesic, superactive Oxyaquic Argiudolls) was 3 to 14 times greater when treated by Mg than by Ca (Dontsova and Norton, 2002). Furthermore, at constant values of SAR, relative *K<sub>sat</sub>* values have been reported to be substantially lower when concentration of Mg on the soil's exchange sites was greater than that of Ca (Curtin et al., 1994b).

The above studies were conducted on natural soils and thus separating the effects of clay mineralogy, organic matter, and Ca vs. Mg dispersion dynamics is difficult. With regards to clay mineralogy, the flocculation values of pure clay minerals (kaolinite, illite, and montmorillonite) were lower than soils having clays of similar mineralogy (Chorom et al., 1994) which follows the findings of Miller et al. (1990) and Churchman et al. (1993) who found that organic matter enhanced soil dispersion. Although natural soils (mineral and organic components) have shown a preference for Ca over Mg on their exchange sites (Curtin et al., 1998; Sposito and Fletcher, 1983; Udo, 1978), these studies were designed to investigate cation selectivity and thus little can



be gleaned about how the ratios of these divalent cations impact soil structure. The objective of our research was to determine the effects of EC, SAR, and Ca/Mg ratios on the dispersion of pure clay minerals (montmorillonite, illite, and kaolinite). The null hypothesis of our research is that EC, SAR, and Ca/Mg ratios will not influence dispersion thresholds.

## **Materials and Methods**

### **Pure clay minerals**

Montmorillonite (Ca-montmorillonite: Cheto, in natural chunk form Gonzales County, Texas), kaolinite (low defect from Washington County, Georgia), and illite (IMt-1, Silver Hill from Montana, Cambrian Shale, characterized by Hower and Mowatt, 1966) were purchased from the Clay Minerals Society and were further modified as noted below.

### **Salt solution preparation**

The SARs of solutions included 1, 5, 12, and 24 with each having Ca/Mg ratios of 1:0, 1:2, 2:1, and 0:1. All cation concentrations henceforth are reported as millimoles of charge per liter unless otherwise noted. For each combination of SAR and Ca/Mg ratio, there were seven EC levels (0, 0.5, 2, 4, 6, 8, 12, and 16 dS m<sup>-1</sup>), all prepared with deionized water (EC ≈ 0). Deionized water was also applied as a treatment for water-dispersible clay determination. Salt solutions with the target EC and SAR values were prepared using anhydrous salts of NaCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub>. The mass of salt needed to make the required solutions was determined by solving the following two equations:

$$\text{SAR} = \text{Na}^+ / [(\text{Ca}^{2+} + \text{Mg}^{2+})/2]^{1/2} \quad (21)$$

$$\text{EC} = \sum (C_i f_i) \quad (22)$$

Where EC is electrical conductivity (μS cm<sup>-1</sup>),  $C_i$  is the concentration of the  $i$ th ionic species in solution ( $i = \text{Na}^+, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{and Cl}^-$ ) (mg L<sup>-1</sup>), and  $f_i$  is the conductivity factor for the  $i$ th ion

species (= 2.13, 2.60, 3.82, and 2.14 ( $\mu\text{S cm}^{-1}$  per  $\text{mg L}^{-1}$ , respectively). The assumption in Eq. (22) is that EC is obtained by summing the products for each ion (Tolgyessy, 1993).

For example, to make a solution with SAR=12, Ca/Mg ratio = 1/2 and EC=4 dS  $\text{m}^{-1}$  (4000  $\mu\text{S cm}^{-1}$ ), the SAR in Eq. (21) was expressed as:

$$12 = x/[(y + 2y)/2]^{1/2} \quad (23)$$

Where  $x$ ,  $y$  are concentrations of Na and Ca, respectively, and the Mg concentration was  $2y$  (Ca/Mg=1/2). Because  $C_i$  in Eq. (22) is in milligrams per liter, ion species ( $C_{\text{Na}}$ ,  $C_{\text{Ca}}$ ,  $C_{\text{Mg}}$ , and  $C_{\text{Cl}}$ ) in solution were converted into these units by:

$$C_{\text{Na}} = 23x \quad (24a)$$

$$C_{\text{Ca}} = 20y \quad (24b)$$

$$C_{\text{Mg}} = 2 \times 12y \quad (24c)$$

$$C_{\text{Cl}} = 35.5 \times (x + y + 2y) \quad (24d)$$

The EC was determined by fitting  $C_{\text{Na}}$ ,  $C_{\text{Ca}}$ ,  $C_{\text{Mg}}$ , and  $C_{\text{Cl}}$  into Eq. (22)

$$\text{EC} = 2.13C_{\text{Na}} + 2.60C_{\text{Ca}} + 3.82C_{\text{Mg}} + 2.14C_{\text{Cl}} \quad (25a)$$

$$4000 = 2.13(23x) + 2.60(20y) + 3.82(24y) + 2.14[35.5(x + y + 2y)] \quad (25b)$$

The values of  $x$  and  $y$  were then determined by solving Eq. (23) and (25b). There were two equations for two unknowns, which makes it possible to calculate the amount of Na ( $x$ ), Ca ( $y$ ) and Mg ( $2y$ ) resulting in  $x$  of 24.04 and  $y$  of 2.68. Finally, the mass of NaCl ( $m_1$ ), CaCl<sub>2</sub> ( $m_2$ ), and MgCl<sub>2</sub> ( $m_3$ ) required to make 1 L of the target solution was determined by:

$$m_1 = x [(1\text{EQ}/1000\text{mmolc})/(1\text{EQ}/\text{mol})] \times M_{\text{NaCl}} \times 1\text{L} \quad (26a)$$

$$m_2 = y [(1\text{EQ}/1000\text{mmolc})/(2\text{EQ}/\text{mol})] \times M_{\text{CaCl}_2} \times 1\text{L} \quad (26b)$$

$$m_3 = 2y [(1\text{EQ}/1000\text{mmolc})/(2\text{EQ}/\text{mol})] \times M_{\text{MgCl}_2} \times 1\text{L} \quad (26c)$$

where  $x$  is Na ( $\text{mmol}_c \text{ L}^{-1}$ ),  $y$  is Ca, and  $2y$  is Mg ( $\text{mmol}_c \text{ L}^{-1}$ ) (in this case  $x = 24.04 \text{ mmol}_c \text{ L}^{-1}$ ,  $y = 2.68 \text{ mmol}_c \text{ L}^{-1}$ ); EQ is equivalent charge;  $M_{\text{NaCl}}$ ,  $M_{\text{CaCl}_2}$ , and  $M_{\text{MgCl}_2}$  are molar masses.

Equations (26a), (26b), and (26c) were further simplified to

$$m_1 = x (10^{-3} \text{ mol L}^{-1}) \times M_{\text{NaCl}} \times 1\text{L} \quad (27a)$$

$$m_2 = y (5 \times 10^{-4} \text{ mol L}^{-1}) \times M_{\text{CaCl}_2} \times 1\text{L} \quad (27b)$$

$$m_3 = 2y (5 \times 10^{-4} \text{ mol L}^{-1}) \times M_{\text{MgCl}_2} \times 1\text{L} \quad (27c)$$

resulting in a calculated mass for NaCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub> of 1.4068, 0.1486, and 0.2544 g, respectively, for creating the target solution (SAR = 12, EC = 4 dS m<sup>-1</sup>, and Ca/Mg=1/2). The SAR and EC of solutions were all rechecked by atomic absorption spectrophotometer (Model 200A; Buck Scientific) and an EC sensor (Sension 378; Hach Co., Loveland, CO, USA), and were determined to be highly acceptable. For example, the EC and SAR of the above example were 3.56 dS m<sup>-1</sup> and 10.38, respectively.

### **Clay calibration and clay dispersion**

Each clay was equilibrated by agitating clay (30 g) and equilibrating solution (150 mL) (1:5 ratio) with the highest targeted EC (16 dS m<sup>-1</sup>) at each respective SAR levels and Ca/Mg ratios for 12 h on a mechanical shaker (225 rev min<sup>-1</sup>), followed by centrifuging for 20 min at 647 ×g. After centrifugation, the supernatant was decanted and discarded, and the process was repeated two more times. After equilibration, the clays were washed four times with 150 mL of 95% ethanol to remove excess ions. After the washings were completed, the equilibrated clays were air dried and ground to pass through a 75 μm sieve. Exchangeable cations (Ca, Mg, or Na) and ESP were then determined following the methods of Warncke and Brown (1998).

For the measurement of dispersed clay, 30 mL of the treatment solution was added to 1 g of equilibrated clay into 50 mL plastic centrifuge tubes (Fisher Scientific). Suspensions were

shaken for 16 h and, after a settling time calculated from Stoke's law (about 93 min), a 5 mL aliquot was collected from a depth of 2 cm (Curtin et al., 1994a). Clay absorbance (optical density) in the aliquot was determined at 640 nm by a spectrophotometer (Spectronic 20+, Thermo Fisher Scientific) which was converted to concentration using calibration curves prepared for each clay mineral (Curtin et al., 1994a).

### **Statistical analysis**

Regression analysis was used to compare the relative dispersed clay percentage for each Ca/Mg ratio for each respective SAR and clay type across all EC values using Proc Nlin in SAS (version 9.3, SAS Institute). If the results from Ca/Mg ratios were not significantly different from each other, all four were combined.

## **Results and Discussion**

### **Solution Ca/Mg ratio effect**

There were no significant differences in dispersion among Ca/Mg ratios for either montmorillonite or kaolinite (Fig. 5 and 6, respectively), but the Ca/Mg ratio of 0/1 was significantly different from the other ratios for SAR 12 for illite (Fig. 7). In agreement with the results of others (Panayiotopoulos et al., 2004; Zhang and Norton, 2002), relative dispersed clay increased with decreasing EC and increasing SAR for both montmorillonite and illite (Fig. 5 and 7); however, variations in EC and SAR did not affect relative dispersed kaolinite (Fig. 6). The influence of EC on the relative dispersed clay depended on SAR levels, where relationships followed sigmoidal ( $y = y_0 + \alpha / (1 + \exp(-(x-x_0)/(\beta)))$ ) at SAR 5, 12 and 24, and hyperbolic decay ( $y = \alpha \beta / (\beta + x)$ ) at SAR of 1 for montmorillonite, and for illite, sigmoidal at SAR 24 and 12 and hyperbolic decay at SAR 5 and 1 (Table 6). For montmorillonite at SAR 24, relative dispersion was greatest when EC was between 0 and 4 dS m<sup>-1</sup> and decreased rapidly as EC increased; for

the remaining SAR values, dispersion was greatest when EC values were  $< 2 \text{ dS m}^{-1}$  (Fig. 5).

Relative dispersed illite was generally less than that of montmorillonite and had dispersion thresholds  $< 2 \text{ dS m}^{-1}$ . Kaolinite had no dispersion at any SAR, EC, or Ca/Mg ratios.

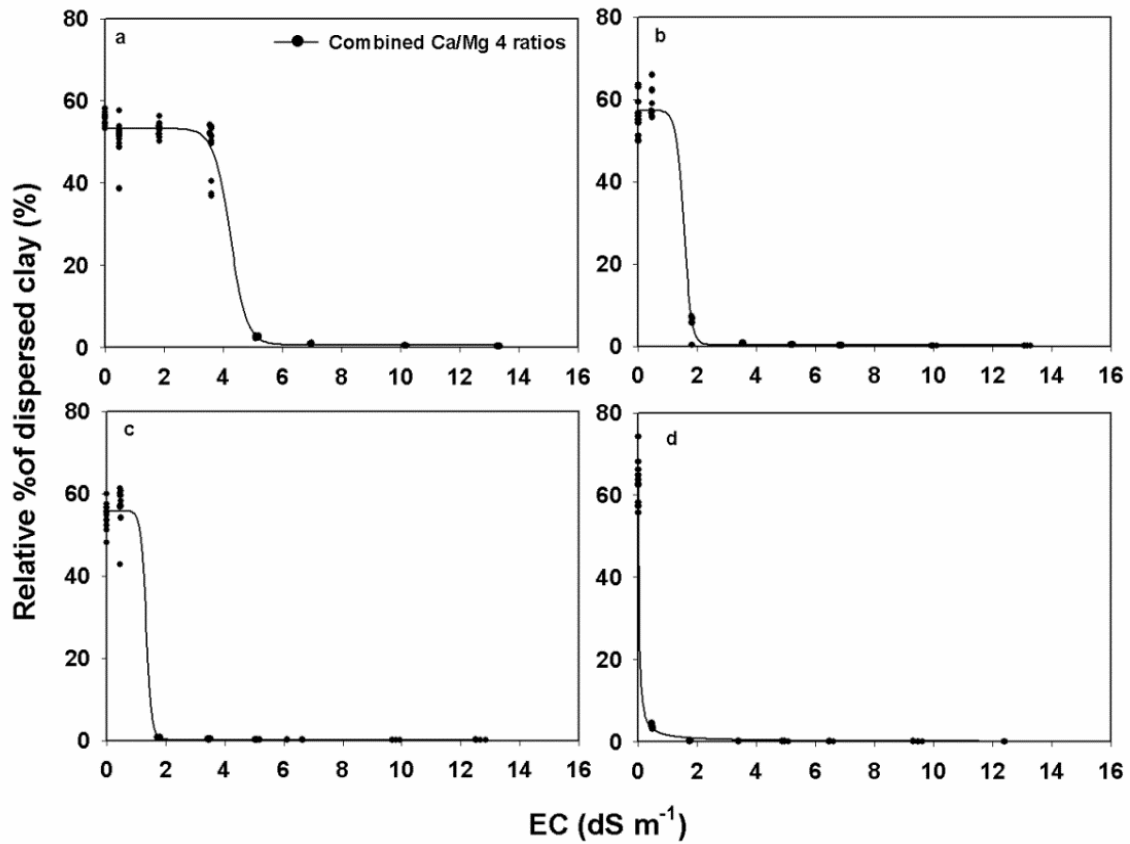


Fig. 5. Dispersed montmorillonite clay as influenced by electrical conductivity (EC) and Ca/Mg ratios (1/0, 2/1, 1/2, and 0/1) at target Na adsorption ratios of (a) 24, (b) 12, (c) 5, and (d) 1. Each fitted model has  $r^2 \geq 0.99$ .

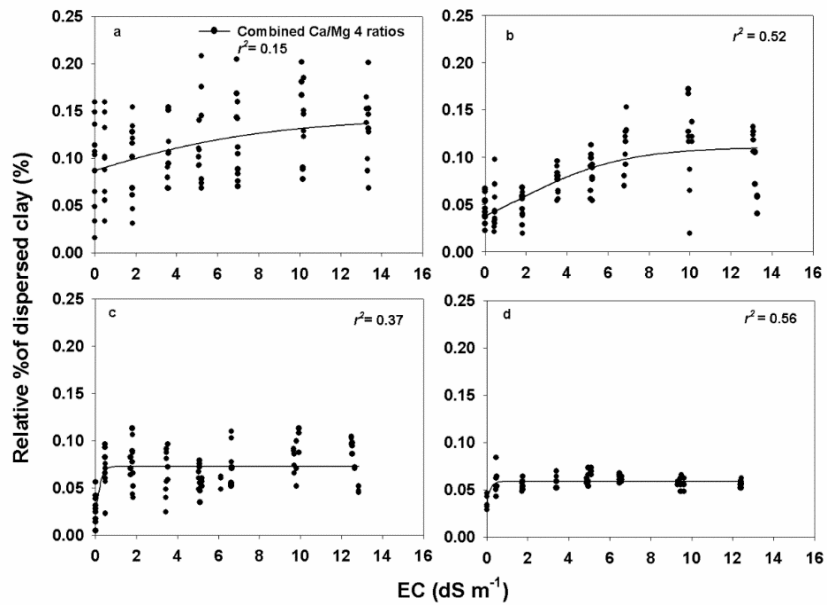


Fig. 6. Dispersed kaolinite clay as influenced by electrical conductivity (EC) and Ca/Mg ratios (1/0, 2/1, 1/2, and 0/1) at target Na adsorption ratios of (a) 24, (b) 12, (c) 5, and (d) 1.

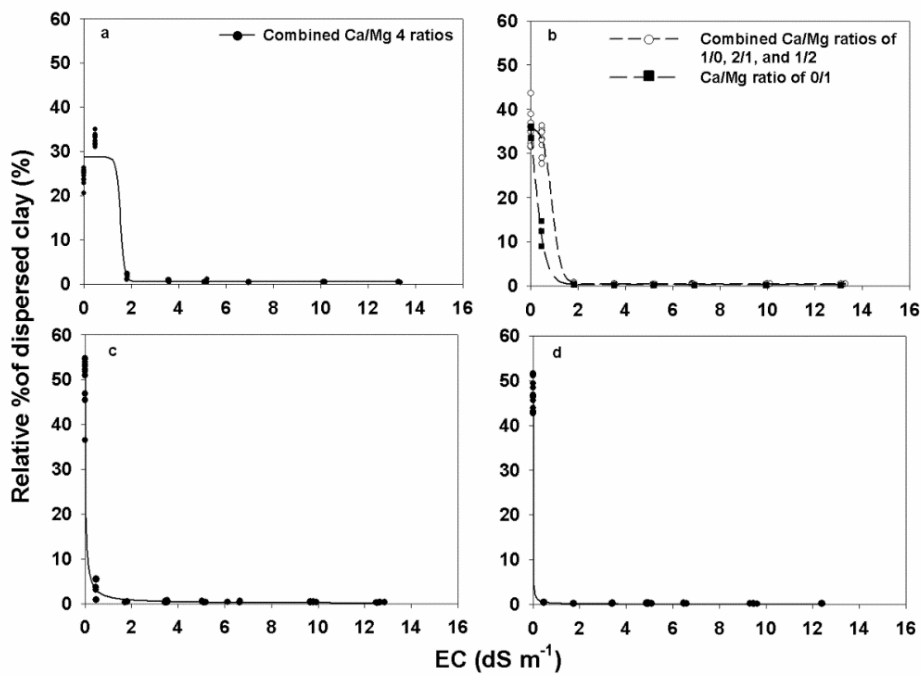


Fig. 7. Dispersed illite clay as influenced by electrical conductivity (EC) and Ca/Mg ratios (1/0, 2/1, 1/2, and 0/1) at target Na adsorption ratios of (a) 24, (b) 12, (c) 5, and (d) 1. Each fitted model has  $r^2 \geq 0.96$ .

Considering dispersion in relation to different SAR, EC, and Ca/Mg ratios, dispersion was the most for montmorillonite, the least for kaolinite and was attributed to structural differences among the different minerals. Montmorillonite has expanding property with a low layer charge, leading to a weak electrostatic force between the 2:1 layers and the interlayer cations and therefore weak forces, together with a large diffuse double layer, permit water entry into interlayer region when Na is predominant on the clay exchange complex (Schaetzl and Anderson, 2005). Kaolinite has little or no isomorphous substitution and a negligible layer charge, and adjacent 1:1 layers are held together by H bonds (Schaetzl and Anderson, 2005). Swelling is a precursor of dispersion, and when montmorillonite is saturated by Ca, clay platelets are held within their flocculation potential and are stable even in deionized water. Dispersion occurs when the solution EC is below the threshold flocculation potential and the diffuse double layers are large (Quirk, 2001). Kaolinite has small double layers on opposing surfaces and hence may not interact, and the slit-shaped pores of kaolinite, due to the small surface area in the microstructure, may not be separated and influenced by exchangeable cations or electrolyte concentrations (Quirk, 2001). The d-spacing of kaolinite (0.71 to 0.73nm) does not vary with the environment due to strong interlayer H bonds, and therefore the adjacent layers don't readily separate and disperse (Essington, 2004).

In our study, Mg did not affect clay dispersion except for illite (SAR 12), which is in agreement with the conclusions of Curtin et al. (1994b), who stated that the effect of Mg on dispersion appeared to be smaller than expected. Although the data are not shown, values of ESP within a clay type were not significantly different at different SAR values, indicating that an exchanger phase preference for Na was consistent across all Ca/Mg ratios. No differences in clay

dispersion across Ca/Mg ratios could support the constant cation selectivity coefficient ( $K$ ) between Ca and Mg reported in Handbook 60 (U.S. Salinity Laboratory Staff, 1954).

The relative dispersed clay for montmorillonite and illite were in agreement with the values obtained by Panayiotopoulos et al. (2004), where the soils with around 20% smectite clay after prolonged shaking, reached a maximum relative dispersion of about 55% at SAR 24. Similar relationships between the amount of dispersed clay and EC were also reported in Curtin et al. (1994a), but the dispersion magnitudes in their study were lower than values in Fig. 5. This may have been due to the pure smectite system in our study compared with natural levels of dominant smectite in their soils. The differences may also be due to the effects of organic matter or metal oxides present in natural soils. For example, organic matter would enhance dispersion because it is sensitive with pH, especially in humid areas, where the soluble organic matter (negatively charged due to small size of molecular-weight acids) form chelation cation bridging between individual clay mineral and organic matter instead of forming links between particles (Churchman et al., 1993). Even though organic matter is thought to increase aggregate stability, it could also enhance dispersion by coating the clay minerals (Churchman et al., 1993). Although organic matter has been shown to have a preference for Ca over Mg, in the absence of organic matter, the value of  $K$  between Ca and Mg may be close to 1 (Curtin et al., 1998; Suarez and Simunek, 1997), which would explain the nonsignificant montmorillonite differences in our study. Similarly, Sposito et al. (1986) found that the Silver Hill illite exhibited no preference in Ca-Mg, Na-Ca, and Na-Mg exchange across ESP ranges of 0 to 30%. Their results support the observations for illite in our study.

Soils in the Northern Great Plain are generally dominated by  $\text{SO}_4^{2-}$ , and when gypsum is the dominant salt, the maximum EC may likely not exceed  $2.2 \text{ dS m}^{-1}$  (Eq. 22). The solutions used



in this study were prepared from  $\text{Cl}^-$ , which resulted in higher EC values than  $\text{SO}_4^{2-}$  salts. Although Suarez and Zahow (1989) showed that the Ca-Mg exchange selectivity coefficient was not significantly different in  $\text{Cl}^-$  vs.  $\text{SO}_4^{2-}$  media for varying ionic strengths, the threshold concentration for soils treated with or dominated by  $\text{SO}_4^{2-}$  salts needs further investigation.

### **Conclusions**

Calcium and Mg ratios on pure montmorillonite and kaolinite across the same SAR did not influence clay dispersion, but 0/1 ratio was significantly different from the other ratios at SAR 12 for illite. The relationship between EC and the relative dispersed clay depended on SARs for montmorillonite and illite and followed formats of sigmoidal and hyperbolic decay, whereas no dispersion was found for kaolinite. The EC levels required to prevent dispersion for montmorillonite were  $< 4$  and  $2 \text{ dS m}^{-1}$  for SAR values of 24, and  $\leq 12$ , respectively. Although other factors will influence dispersion and swelling, these target values should be considered when the goal is to improve water movement and soil structure.

### **Acknowledgments**

The material is based on work supported by the USDA-NRCS under the Conservation Innovation Grants program.

Table 6. Models for the relationship between percentage of dispersed clay and electrical conductivity and their parameters following sigmoidal ( $y = y_0 + \alpha / \{1 + \exp [-(x-x_0)/\beta]\}$ ) or hyperbolic ( $y = \alpha\beta / [\beta + x]$ ). All Ca/Mg ratios were not significantly different ( $P \leq 0.05$ ) for the respective clay type and Na adsorption ratio (SAR) and were combined unless noted.

Clay type	Target sodium adsorption ratio	Model equation	Parameter			
			$\alpha$	$\beta$	$y_0$	$x_0$
Montmorillonite	24	$y^\dagger = 0.61 + 52.6 / \{1 + \exp [-(x^\ddagger - 4.24) / (-0.28)]\}$	52.6	-0.28	0.61	4.24
	12	$y = 0.31 + 57.1 / \{1 + \exp [-(x - 1.54) / (-0.13)]\}$	57.1	-0.13	0.31	1.54
	5	$y = 0.21 + 55.7 / \{1 + \exp [-(x - 1.35) / (-0.09)]\}$	55.7	-0.09	0.21	1.35
	1	$y = 1.91 / (0.03 + x)$	63.6	0.03		
Illite	24	$y = 0.53 + 28.2 / \{1 + \exp [-(x - 1.55) / (-0.09)]\}$	28.2	-0.09	0.53	1.55
	12 <sup>‡</sup>	$y = 0.45 + 35.6 / \{1 + \exp [-(x - 0.91) / (-0.18)]\}$	35.6	-0.18	0.45	0.91
	12 <sup>§</sup>	$y = 0.24 + 64.2 / \{1 + \exp [-(x - 0.05) / (-0.27)]\}$	64.2	-0.27	0.24	0.05
	5	$y = 1.51 / (0.03 + x)$	50.4	0.03		
	1	$y = 0.47 / (0.01 + x)$	46.9	0.01		
Kaolinite	24	$y = 0.14 / \{1 + \exp [-(x + 2.23) / 5.01]\}$	0.14	5.01		-2.23
	12	$y = 0.11 / \{1 + \exp [-(x - 1.63) / 2.54]\}$	0.11	2.54		1.63
	5	$y = 0.07 / \{1 + \exp [-(x - 0.08) / 0.15]\}$	0.07	0.15		0.08
	1	$y = 0.06 / \{1 + \exp [-(x + 0.07) / 0.14]\}$	0.06	0.14		-0.07

<sup>†</sup>  $y$  is dispersed clay percentage (%);  $x$  is electrical conductivity ( $\text{dS m}^{-1}$ ).

<sup>‡</sup> Model was determined when the Ca/Mg ratios of 1/0, 2/1, and 1/2 were combined.

<sup>§</sup> Model was determined only for a Ca/Mg ratio of 0/1, which was significantly different ( $P \leq 0.05$ ) from other ratios at this SAR.

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**PAPER 3. FIELD CAPACITY WATER AS INFLUENCED BY NA AND EC:  
IMPLICATIONS FOR SUBSURFACE DRAINAGE**

**Abstract**

Subsurface-tile drainage is designed to remove gravitational water and soluble salts from the soil-root zone. However, soil swelling, as influenced by soil Na and electrical conductivity (EC), will reduce saturated hydraulic conductivity. The objective of this research was to determine the influence of Na and EC on the amount of water retained at field capacity (- 33 kPa), in northern Great Plains tile-drained Na-affected soils. The impact of six EC levels on the amount of water retained in the soil at field capacity was determined in subsurface soil collected from four sodium-affected soils. Field capacity water (gravimetric water content) for all soils increased with increasing and decreasing sodium absorption ratio (SAR) and EC, respectively. For example, at an EC of 4 dS m<sup>-1</sup>, the amount of water retained at field capacity increased from 0.23 to 0.31 g g<sup>-1</sup> as SAR increased from 7 to 28, respectively. For the same soil, field capacity water decreased from 0.31 to 0.18 g g<sup>-1</sup> when EC increased from 0.5 to 15 dS m<sup>-1</sup> at SAR 24. In general, across all SAR values, an EC greater than 4 dS m<sup>-1</sup> was required to prevent swelling. However, for soils with high natural salinity, no significant difference was observed for field capacity water using the above methods; the presence of calcite in these soils may have reduced the potential for water retention and may have reduced field capacity values. Therefore, to maintain drainage performance in sodium-affected soils one should regularly monitor Na and EC within the soil profile so that EC values do not fall below critical threshold values.

**Introduction**

Many sodium-affected soils have low to moderate plant production potentials, depending on the location of the sodium-rich horizon within the profile. In the Northern Great Plains of the

USA excessive annual precipitation resulting in wetter spring soils and higher groundwater levels, in combination with increased commodity prices (Hellerstein and Malcolm, 2011) have resulted in farmers increasing the installation of subsurface tile drainage. However, there are over 4.7 million acres (1.9 million ha) of sodium-affected soils within this region (J. Brennan, personal communication, NRCS North Dakota, 2008) and since sodium-affected soils are interspersed with high-productivity soils, these too are being tiled. The tile drainage of Na affected soils can result in clay dispersion and reduced water flow through soils (Sumner and Naidu, 1998). Sodium induced swelling and dispersion are more severe in 2:1 swelling clays (i.e. montmorillonite) that are most common in the northern Great Plains, compared to 1:1 or 2:1 non-swelling clays (Curtin et al., 1994; He et al., 2013).

Swelling is associated with the hydration of clays, and when the force of hydration is greater than electrostatic attractive forces, clay sheets layers separate and the distance between them increases (Foster, 1954; Sumner and Naidu, 1998). Dispersion occurs when repulsive forces continue to be greater than attractive forces, clay particles separate into individual particles (Sumner and Naidu, 1998). The hydration of Na forces clay layers apart and results in a weak bridge between clay layers due to their low charge, so bigger quasicrystals (QC) of clay break down into smaller ones with Na staying on external surface of (Foster, 1954; Grim, 1968; Pils et al., 2007). As more water enters the soil system the cation chemical potential in the clay interlayers and bulk solution become lower than that on the clay mineral surface. Therefore, cations have the potential to diffuse into the adjacent bulk solution by diffusive forces (as the repulsive forces) in order to reduce the enthalpy of the system (Engel and Reid, 2012). When this process continues, clays are more widely separated, i.e. dispersed, and finally a new equilibrium will be reached after attractive and repulsive forces equilibrate. However, the Na induced shrink

and swell path is not reversible in situations of dominant water loss compared to the shrink and swell path of normal swelling soils (Tripathy et al., 2002).

The specific mechanism for swelling is related to both Na and electrical conductivity (EC) (Essington, 2004). Swelling reduces soil pore size and therefore reduces saturated hydraulic conductivity ( $K_{sat}$ ) (Ben-Hur et al., 2009; Cass and Sumner, 1982) and aeration (Sumner and Naidu, 1998). In addition, swelling increases gravimetric water retention at field capacity (-33 kPa), increases the soil plastic and liquid limits (Grim, 1968; Kyei-Baffour et al., 2004), decreases trafficability (Earl, 1997), and may increase energy requirements for soil tillage (Guarnieri et al., 2005). To prevent further land degradation, improved knowledge of soil swelling and water retention at field capacity is needed. The objective of this research was to determine the influence of Na and EC on the amount of water retained at field capacity (-33 kPa), in Northern Great Plains tile drained, Na-affected soils.

## **Materials and Methods**

### **Soil samples**

Soil samples were obtained from four different soil series from eastern North Dakota (Table 7). The series were Exline (Fine, smectitic, frigid Leptic Natrudolls), Stirum (Coarse-loamy, mixed, superactive, frigid Typic Natraquolls), Ryan (Fine, smectitic, frigid Typic Natraquerts) and Bearden-saline phase (Fine-silty, mixed, superactive, frigid Aeric Calciaquolls). All samples were collected from the 0 to 15, 15 to 30, 30 to 60, and 60 to 90 cm depths. After collection, the soils were air-dried, ground, and sieved (< 2 mm).

Particle size distribution was determined using the hydrometer method (ASTM 152-H Soil Hydrometer, H-B Instrument Co.) following the procedure of Gee and Bauder (1986). Saturated paste extracts for soil were prepared following the standard method described by U.S.



Salinity Laboratory Staff (1954). The pH, ECe and soluble cations (SAR<sub>e</sub>) were determined from saturated paste extracts and were subsequently analyzed using a pH meter (13-636-AB15B, Fisher Scientific), EC meter (Sension 378; Hach Co., Loveland, CO, USA), and by atomic absorption spectroscopy (AAS) for calculation of SAR (Model 200A; Buck Scientific, Inc.). Soil cation exchange capacity (CEC) and exchangeable sodium percentage (ESP) were calculated (USDA-NRCS, 2011). Total calcite present in soils was determined from a modified version of Sherrod et al. (2002). Mineralogy of the clay fractions was determined for the four soils with the greatest SAR using X-ray diffraction (XRD) (Whittig and Allardice, 1986) (Table 7). The general analysis can be found in Appendix Fig. B1 to B4.

### **Field capacity water**

In this study, the field capacity water (FCW) will be used as an indicator for swelling (Curtin et al., 1994). Solutions were prepared with the same SAR simulating the SAR<sub>e</sub> of each depth of soil. At each SAR, seven EC levels (0, 0.5, 1, 2, 4, 8, and 15 dS m<sup>-1</sup>), were prepared using NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, and deionized (DI) water. Solutions were prepared following He et al. (2013) based on Eq. (28) and (29):

$$\text{SAR} = \text{Na}^+ / [(\text{Ca}^{2+} + \text{Mg}^{2+})/2]^{1/2} \quad (28)$$

$$\text{EC} = \sum (C_i f_i) \quad (29)$$

where the assumption in Eq. (29) is that EC is obtained by summing product values of each ion (*i*) concentration (*C<sub>i</sub>*) of species *i* in solution (Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Cl<sup>-</sup>) (mg L<sup>-1</sup>) with the conductivity factor (*f<sub>i</sub>*) for ion species, where *f<sub>i</sub>* equals 2.13, 2.60, 3.82, and 2.14 (μS cm<sup>-1</sup> per mg L<sup>-1</sup>), respectively, and the unit for EC is μS cm<sup>-1</sup> (Tolgyessy, 1993). During preparation, the Ca/Mg ratio of 1:1 was adopted which may be different from the actual Ca/Mg ratios in actual soil samples since the Ca/Mg ratio was found to have no significant influence on pure

montmorillonite dispersion (He et al., 2013). The SAR and EC of solutions were all rechecked by AAS (Model 200A, Buck Scientific) and conductivity meter (Sension 378, Hach Co.), respectively. The actual EC was very similar to the target EC at low values, varying only slightly, but EC varied higher at high EC (Marcus and Hefter, 2006). For example, for target EC of  $15 \text{ dS m}^{-1}$  the actual value was  $12.1 \pm 0.35$ , while for target EC of  $1 \text{ dS m}^{-1}$ , the value was  $0.97 \pm 0.02$ . Actual SAR of the solution was very similar to the target SAR.

The influence of SAR and EC on FCW was determined by measuring the amount of water imbibed at an applied pressure of  $-33 \text{ kPa}$ , which is a gravimetric water content (Curtin et al., 1994). Each EC solution at the respective SAR was added to the ceramic plate to the height of the soil-containment ring ( $5 \text{ cm}$  diameter, height of  $1 \text{ cm}$ ) and allowed to saturate for  $20 \text{ h}$ . Pressure ( $33 \text{ kPa}$ ) was then applied for  $48 \text{ h}$  followed by determination of gravimetric soil water content. For each soil and EC-SAR combination, four replications were used. The ceramic plate was washed between runs using deionized water.

Another solution was prepared having SAR of  $0$  and EC of  $15 \text{ dS m}^{-1}$  and was used as a reference solution for each soil and depth. This solution was used to best describe FCW if the soils were not impacted by Na. The gravimetric soil water content was determined as above.

To determine the exchangeable cations and ESP in the high EC soils (Ryan and Bearden soils) one depth from each series was washed of naturally occurring salts (Table 7). Washing was accomplished by shaking using  $50 \text{ g}$  of soil with  $150 \text{ mL}$  of washing solution (SAR =  $0$  and EC =  $15 \text{ dS m}^{-1}$ ) for  $12 \text{ h}$ . The solution was centrifuged at a relative centrifuge force of  $670 \times g$  for  $20$  minutes. The supernatant was discarded and the entire process repeated three times. After equilibration, soil was washed three times with  $150 \text{ mL}$  of  $95\%$  ethanol to remove excess ions. Finally, the equilibrated soil was air-dried and ground to pass through a  $75 \mu\text{m}$  sieve.

Exchangeable cations (Ca, Mg, or Na) and ESP were determined following the methods of Warncke and Brown (1998).

### **Statistical analysis**

Analysis of variance (ANOVA) was performed using the PROC ANOVA procedure in SAS 9.3 (SAS Inc., Cary, NC). Effect of successive values of EC at the same SAR and the overall SAR effect for different depth of soil FCW at the same EC were compared by SAS by using least significant difference (LSD) to test for differences. The difference of FCW obtained at respective SAR and EC of 15 dS m<sup>-1</sup> solution were compared to that at reference line of each depth of soil by a t-test using MINITAB Student Release 14 (1972 - 2003 Minitab Inc.).

## **Results and Discussion**

### **Soil properties**

The main differences in native soil properties were clay content and EC where the Exline and Stirum soils were lower in both properties (Table 7). Sodium adsorption ratios generally increased as depth below the soil surface increased and ranged from 2.7 to 27.6 across all soils. Based on the CEC and XRD analyses the dominant clay mineral in each of the four samples was smectite (montmorillonite). Using Handbook 60 (U.S. Salinity Laboratory Staff, 1954) the Exline, Stirum, Ryan, and Bearden soils were generally classified as sodic, sodic, saline-sodic, and saline, respectively.

### **Effect of electrical conductivity**

Although not all of the reference-solution FCW values were significantly different from FCW obtained at EC of 15 at each respective SAR (Table 8), the differences between respective depths were small. Therefore, water holding capacity at FCW can help to indicate the degree of swelling using the FCW obtained at an EC = 15 dS m<sup>-1</sup>, at least up to the SAR values in Table 7.

Table 7. Taxonomic classification and physical and chemical properties of the studied soils.

Soil Series	Depth cm	Soil texture			Soil saturated paste extract				Total CaCO <sub>3</sub> %	CEC cmol kg <sup>-1</sup>	ESP %	XRD of minerals <sup>‡</sup>
		Sand g kg <sup>-1</sup>	Silt g kg <sup>-1</sup>	Clay g kg <sup>-1</sup>	SP <sup>†</sup> %	EC <sub>e</sub> dS m <sup>-1</sup>	pH <sub>e</sub>	SAR <sub>e</sub>				
Exline	0-15	575	226	200	48.4	1.47	8.0	7.38	0.12	12.7	6.36	
	15-30	557	243	200	46.1	1.70	8.4	14.1	0.08	11.3	10.6	
	30-60	649	152	200	49.3	2.27	8.8	23.9	0.86	9.2	28.2	
	60-90	392	245	363	73.3	2.12	8.8	27.6	15.1	12.7	20.6	Sm, Kao, I, Qz
Stirum	0-15	629	184	188	46.7	1.36	8.3	4.71	1.75	11.5	4.47	
	15-30	644	119	238	44.3	1.33	8.7	9.30	1.92	11.8	10.1	
	30-60	661	114	225	36.8	1.60	8.6	11.6	1.58	8.5	14.2	
	60-90	573	177	250	42.6	1.32	8.9	17.5	10.9	7.5	18.5	Sm, Kao, I, Qz
Ryan	0-15	84.0	389	528	84.6	9.60	8.0	10.0	0.5	25.3	4.60	
	15-30	45.0	300	655	86.9	13.0	8.0	12.0	1.23	25.0	8.03	
	30-60	36.0	315	650	79.6	12.5	7.9	13.4	15.1	20.7	9.29	Sm, Kao, I, Qz
	60-90	47.0	303	650	83.2	11.6	7.9	13.2	16.1	20.2	10.4	
Bearden	0-15	159	591	250	57.2	10.2	7.7	3.05	0.95	21.3	2.81	
	15-30	139	606	255	57.4	9.25	7.7	3.47	1.32	20.3	2.56	Sm, Kao, I, Qz
	30-60	103	622	275	46.4	7.79	7.8	3.16	17.4	12.4	2.92	
	60-90	58.0	567	375	61.2	6.73	7.8	2.70	15.7	14.1	3.72	

† SP, Saturation percentage of saturated paste.

‡ Sm, Smectite; Kao, Kaolinite; I, Illite; Qz, Quartz.

Water adsorption increased as EC decreased and a graphical representation of this relationship for two depths of the Exline soil can be seen in Fig. 8. Here, from a high to low EC, at a SAR of 6.57 there was a 14% increase in FCW whereas at an SAR of 26.4 there was a 47% increase. Although exceptions exist, the Exline and Stirum soils had significantly different ( $P < 0.001$ ) FCW across EC for the same depth of soil at the same SAR (Table 8). These results were similar to those of Curtin et al. (1994) who reported that in 5 of 6 southern Saskatchewan Canada soils water retention had a greater response to SAR than EC.

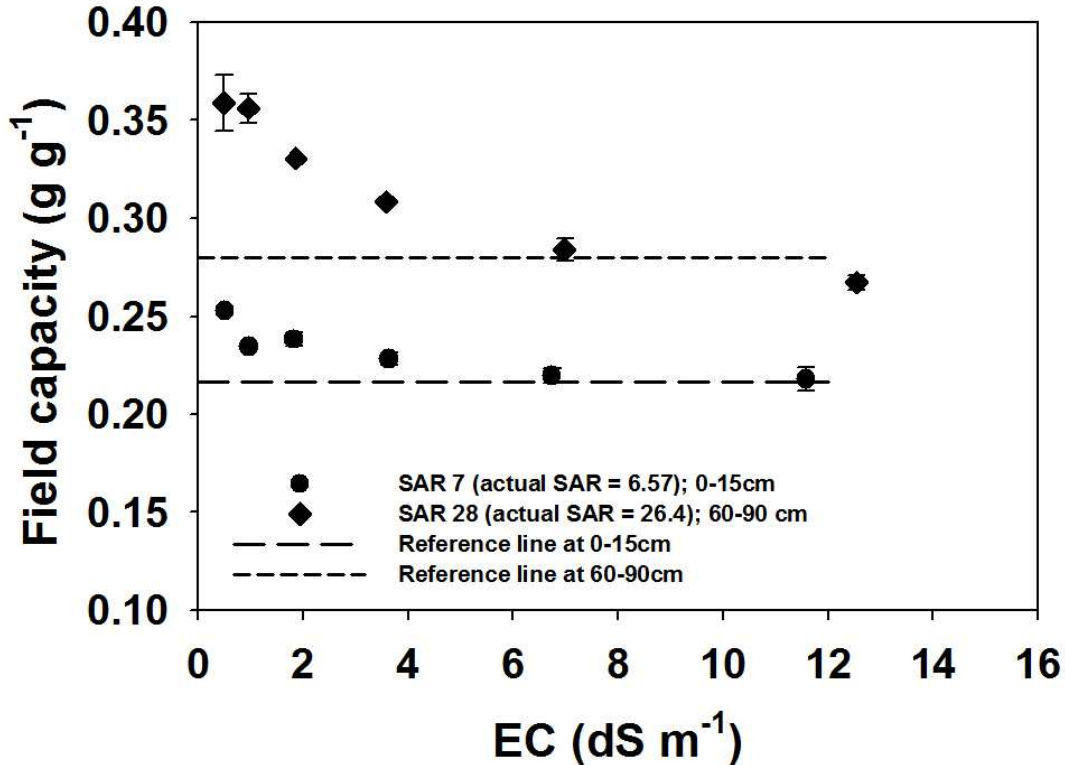


Fig. 8. Relationship between field capacity and solution EC for Exline soil from two depths.

Conversely, fewer differences existed for the Ryan and Bearden soils, which may have been due to their higher salt levels or the inability to reduce their natural soluble salt

concentrations (Table 7) during the saturation step. When salts were washed from the Ryan and Bearden soils the effect of solution EC on water adsorption was significantly greater than before salts were washed out (Fig. 9). This indicates that high levels of EC would be beneficial for prohibiting clay separation and extra water imbibing for soils with high SAR. The result is consistent with the results from Ben-Hur et al. (2009) where deionized water resulted in a greater swelling value than saline water for both clay and loamy-sand soils. However, high EC is normally not desirable for growing most plants (Ogle et al., 2004).

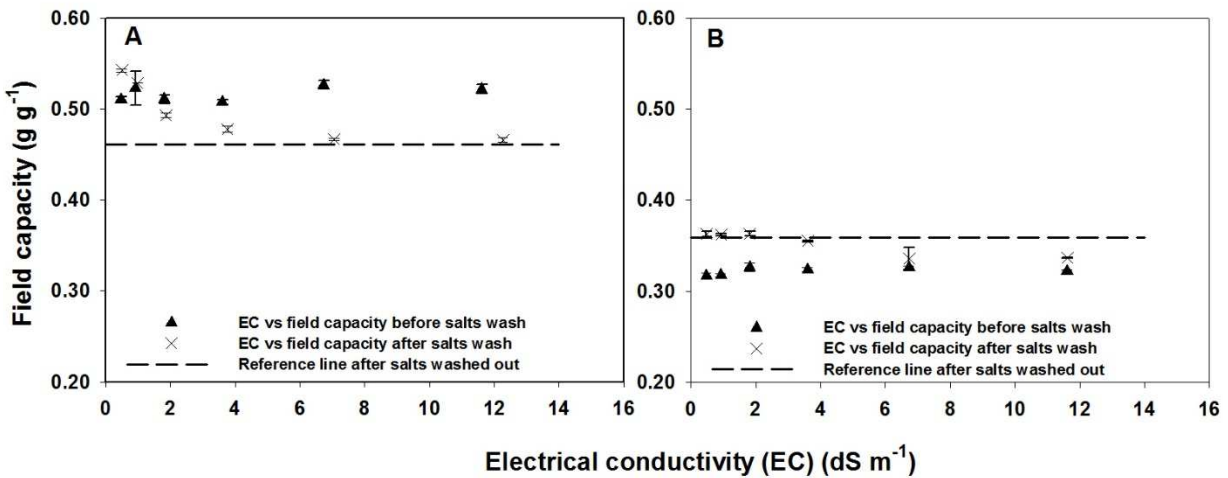


Fig. 9. Change of field capacity with EC before and after salts were washed out for A: Ryan soil at depth of 15-30 cm and B: Bearden soil at depth of 60-90 cm.

The removal of salts using the washing steps could be considered as a drainage simulation, and similar to the findings of Bao et al. (2013) who observed a decline of soil EC due to subsurface drainage. As noted by many authors, each soil has threshold concentrations (the minimum salt solution to prevent soil from dispersion) of EC and SAR, so that swelling and/or dispersion may not occur (He et al., 2013; Panayiotopoulos et al., 2004; Quirk and Schofield, 1955). In our study the threshold EC across all SAR values was about 4 dS m<sup>-1</sup> (Table 8).

Changes in water holding capacity are attributed to clay swelling because at low EC values the Na present on external clay surfaces begins to migrate into the clay-sheet interlayers of quasicrystals of smectite whereby it replaces/demixes other monovalent and divalent cations (Pils et al., 2007). The small size of Na allows it to reside in the pseudo-hexagon of clay silicon tetrahedron sites causing an increase in the “water net” thickness and swelling (Grim, 1968; Velde and Meunier, 2008). Disruption of the “water nets” and reduction of soil swelling occurs when Ca is present and when the EC of the soil solution is high, both conditions required to decrease the thickness of the diffuse-double layer (Grim, 1968; Pils et al., 2007). The decreasing sizes of the quasicrystals allow for more swelling and imbibed water, and may lead to dispersion (Pils et al., 2007).

The effect of EC on FCW in our study indicates a reduction in soil condition that may occur during tile drainage. For example, Pons et al. (2000) showed that the porosity of a sodium-affected soil decreased (no macropores), which in turn inhibited early winter wheat (*Triticum aestivum* L.) root development. In addition, clay swelling in deeper soil horizons together with dispersion adversely affects soil structure for water movement and drainage performance (Dikinya et al., 2006).

### **Chemical factors (SAR and CaCO<sub>3</sub>) effect**

Sodium adsorption ratios had significantly different ( $P < 0.05$ ) effects on FCW at different soil depths, where FCW increased with SAR (Fig. 10). This effect was most noticeable for the Exline and Stirum soils which also had the greatest ranges in SAR (Table 9). The SAR effect was decreased as the EC of the solution increased from 0.5 to 15 dS m<sup>-1</sup> (Fig. 10). However, the effect of SAR was not noticeable for Ryan and Bearden soils at constant EC. In order to compare to relatively healthy soils, the FCW at reference treatments were compared

with that treated by highest EC ( $15 \text{ dS m}^{-1}$  in our study) and found to be no significant difference for most of soils (Table 9). This indicates that different values of FCW at the highest and lowest EC of the same soil can be viewed as estimation of magnitude of swelling.

The presence of  $\text{CaCO}_3$  may also influence water absorption for soils. For example, the 30 to 90 cm depths for the Ryan and Bearden soils had much greater concentrations of  $\text{CaCO}_3$  than the upper depths of these two soils (Table 7). The FCW of the deeper depths was generally significantly lower than the upper soil depths with only  $\text{CaCO}_3$  being greatly different (Table 8). Calcium hydroxide ( $\text{Ca(OH)}_2$ ) is commonly used in civil engineering projects to stabilize swelling soils through “pozzolanic activity” (Bell, 1996; Guney et al., 2005). In this pozzolanic activity the reaction occurs at a very high pH (greater than pH 12) due to  $\text{Ca(OH)}_2$  (Guney et al., 2005), which is not naturally found in northern Great Plains soils. Due to the low solubility of  $\text{CaCO}_3$  it is unlikely that EC will be increased more than about  $0.3 \text{ dS m}^{-1}$  at saturation to effectively control excessive swelling, as was hypothesized by Keren and Ben-Hur (2003). The low solubility of  $\text{CaCO}_3$  is a major factor in why it is not regularly used for sodium-affected soil management. The likely reason why  $\text{CaCO}_3$ -enriched soils had lower FCW than the upper soils was due to pore soil particle cementation (Cheng et al., 2013). At field capacity or lower water saturation concentrations,  $\text{CaCO}_3$  bridges across soil particles, increasing soil stability, and thus likely minimizing swelling. Further exploration of  $\text{CaCO}_3$  bridging may allow for increased use of calcium carbonate ( $\text{CaCO}_3$ ) for sodium-affected soil management, and thus increased trafficability across these problem soils.



Table 8. Gravimetric field capacity water content at 33kPa under each combination of SAR and EC.

Soil	Depth	Target SAR <sup>‡</sup>	Target electrical conductivity values (dS m <sup>-1</sup> ) <sup>†</sup>					
			0.5	1	2	4	8	15
	cm		-----Water content (g g <sup>-1</sup> )-----					
Exline	0-15	7	0.25a <sup>§</sup> D <sup>#</sup>	0.23b D	0.24b C	0.23c C	0.22d B	0.22d B
	15-30	14	0.28a C	0.26b C	0.25b C	0.23c C	0.22c B	0.19d C
	30-60	24	0.31a B	0.28b B	0.27c B	0.25d B	0.21e C	0.18f C
	60-90	28	0.36a A	0.36a A	0.33b A	0.31c A	0.28d A	0.27e A
Stirum	0-15	5	0.19a C	0.19a BC	0.20a A	0.19a A	0.19a A	0.19a A
	15-30	9	0.22a B	0.20ab B	0.20ab A	0.18bc A	0.18bc A	0.17c B
	30-60	12	0.18a D	0.17b C	0.17b B	0.15c B	0.15c B	0.14d C
	60-90	18	0.24a A	0.24a A	0.20b A	0.19c A	0.18c A	0.16d B
Ryan	0-15	10	0.53ab A	0.53ab A	0.54a A	0.52bc A	0.52bc B	0.51c B
	15-30	12	0.51cd B	0.52ab A	0.51bcd B	0.51d A	0.53a A	0.52abc A
	30-60	14	0.43a C	0.43a B	0.43a C	0.43a B	0.43a C	0.43a C
	60-90	13	0.44bc D	0.45ab C	0.45a D	0.44bc B	0.44ab D	0.44c D
Bearden	0-15	3.0	0.36a A	0.35bc A	0.35bc A	0.34c A	0.35b AB	0.35bc B
	15-30	3.5	0.36ab A	0.35b A	0.36ab A	0.34b A	0.37a A	0.36ab A
	30-60	3.2	0.30a C	0.29ab C	0.28bc C	0.28cd C	0.27d C	0.27d D
	60-90	2.7	0.32c B	0.32c B	0.33a B	0.32ab B	0.33a B	0.32b C

† Target EC values were used here since variation of actual EC values occurred for all soils and depth compared to target EC.

‡ Target SAR values were produced to match original soil SARe.

§ Different lowercase letters in each row indicate that the field capacity was significantly different between EC values at the same SAR.

# Different uppercase letters in each column for each soil indicate that the field capacity was significantly different between SAR values in different depths at the same EC.

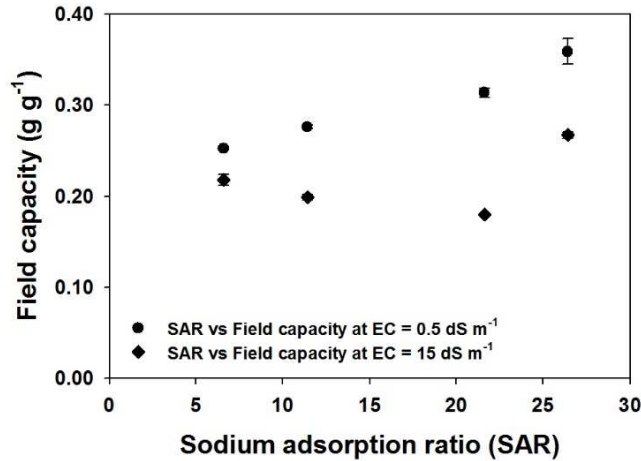


Fig. 10. Example relationship between field capacity and solution SAR for the Exline soil from two EC levels of 0.5 and 15 dS m<sup>-1</sup>.

Table 9. Comparison of field capacity water (FCW) obtained at the highest EC of each depth (SAR = X, EC = 15 dS m<sup>-1</sup>) to FCW obtained at reference solution (SAR = 0, EC = 15 dS m<sup>-1</sup>).

Soil	Depth	FC obtained at EC of 15dS m <sup>-1</sup>	FC at reference solution	Difference	<i>P</i> value
	cm	-----g g <sup>-1</sup> -----			
Exline	0-15	0.243	0.219	0.025	0.005* <sup>†</sup>
	15-30	0.188	0.203	-0.015	0.414
	30-60	0.180	0.190	-0.010	0.108
	60-90	0.267	0.280	-0.013	0.006*
Stirum	0-15	0.191	0.192	-0.001	0.883
	15-30	0.172	0.165	0.006	0.351
	30-60	0.142	0.136	0.005	0.195
	60-90	0.159	0.173	-0.015	0.093
Ryan	0-15	0.51	0.539	-0.028	0.008*
	15-30	0.522	0.504	0.018	0.05
	30-60	0.428	0.511	-0.083	0.001*
	60-90	0.437	0.539	-0.102	0.000*
Bearden	0-15	0.347	0.348	-0.001	0.905
	15-30	0.357	0.351	0.006	0.474
	30-60	0.272	0.326	-0.054	0.007*
	60-90	0.322	0.431	-0.11	0.000*
Ryan salts washed	15-30	0.466	0.461	0.005	0.079
Bearden salts washed	60-90	0.337	0.354	-0.017	0.030*

<sup>†</sup> Asterisks indicates that the difference is significantly different at *P* = 0.05.

## **Implications for subsurface drainage**

Results in our study support that both SAR and EC are responsible for swelling, which has been stated by many authors (Ben-Hur et al., 2009; Curtin et al., 1994; Sumner and Naidu, 1998). In soils where SAR increased with soil depth, which was consistent with the findings of McClelland et al. (1959) for many North Dakota soils, swelling may help to explain the phenomenon that the drainage performance in some sodium-affected soils decreases after several growing seasons (Cihacek et al., 2012; Hopkins et al., 2012). Drainage performance problems may occur in the affected horizons and may greatly reduce the drainage of precipitation-derived gravitational water. However, upward moving groundwater may still be removed without restrictions because EC generally remains high at deep depths in Aquifer in the Sheyenne delta (Baker and Paulson, 1967).

This research showed that each soil-Na level has a threshold EC where water movement is not restricted, stability is maintained, and swelling is minimized in agreement with the findings by Quirk and Schofield (1955). Considering Fig. “7, 8, and 9” in Shabtai et al. (2014), the reduction in  $K_{sat}$  is mainly dominated by swelling and partially by dispersion, both related to ESP and EC. In their study, when swelling increased from 36 to 97% the saturated hydraulic conductivity ( $K_{sat}$ ) decreased from 400 to 0 mm hr<sup>-1</sup>. Shabtai et al. (2014) and Zhu et al. (2013) had similar results and reported in bentonite and smectitic clays where  $K_{sat}$  decreased from 3.2 to 0.7x10<sup>-6</sup> mm hr<sup>-1</sup> with the increase of final swelling pressure from 3 to 4.5 MPa. Using the relationships developed by Curtin et al. (1994) and Shabtai et al. (2014), swelling by as little as 16 to 25% can decrease  $K_{sat}$  to one third of the original value. Therefore, results from above studies of Shabtai et al. (2014) and Zhu et al. (2013) were used to estimate the effect of swelling on water movement ( $K_{sat}$ ) in our study. It was found that if tile drainage was responsible for

decreasing EC from 4 to 0.5 dS m<sup>-1</sup> and SAR remained constant at 14 (Exline soil) (Table 8), Ksat can be predicted to decrease to about one third of original value. Although this relationship is not likely to be linear, decreasing EC without decreasing the relative ratio of Na in soil will undoubtedly decrease water movement and expected tile performance.

However, limitations may exist for applying this study's laboratory results to the field settings, and more environmental factors have to be considered to allow for field assessment. For example, the freeze and thaw process in northern Great Plains would result in accumulation of winter deposits of salts in the freezing zone from the shallow water table and leaching of salts in spring snow melt (Fullerton and Pawluk, 1987; Miller and Brierley, 2011). The resulting redistribution of salts would be expected to influence EC, soil water retention, and therefore drainage. The spatial variability in soil series and textures in the field is another factor that will influence water movement (Ben-Hur et al., 2009), as would crops that were planted and their rooting depths (Ghane et al., 2012). Bulk density, influencing water storage and permeability, may change and decrease after many years as result of tile drainage as found by Bucur and Moca (2012).

### **Conclusion**

Soil Na and soluble salt concentrations were found to be two important chemical factors influencing FCW, an indicator of swelling in our study, where FCW generally increased as SAR increased and EC decreased. However, an increase in percent CaCO<sub>3</sub> appears to help decrease the likelihood of the soil imbibing excess FCW, irrespective of EC. These results indicate that maintaining an EC level above 4 dS m<sup>-1</sup> may prevent swelling. In addition, if tile drainage removes soluble salts from those soils that have an SAR greater than 5, the FCW may increase and thus decrease the rate of water movement. Long-term management plans for these high-risk

soils should include chemical amendments such as gypsum, elemental S, or possibly agricultural lime as a means to maintain or increase EC, provide  $\text{Ca}^{2+}$ , and/or increase trafficability.

### **Acknowledgments**

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**PAPER 4. ENVIRONMENTAL AND SOIL FACTORS FOR PREDICTIONS WHERE  
AMENDMENTS FOR SODIC SOILS SHOULD BE APPLIED: A CASE STUDY ON A  
NEARLY-LEVEL LANDSCAPE**

**Abstract**

High spatial variation of sodicity can lead to inadvertent over- and under-application of amendments such as gypsum which is why site-specific management of sodic soils is difficult. The objective of this study was to characterize the spatial variation of Na and its relationship to environmental (elevation using RTK GPS and topographic wetness index (TWI)) and soil factors (EC<sub>1:1</sub>, pH<sub>1:1</sub>, Na%, ECa, and dispersion) to determine the likelihood of making site-specific amendment recommendations for sodic soil management. A grid sampling pattern having 544 geo-referenced sites in a 8.1 ha sodic soil study area in North Dakota was used for this case study. At each site soil samples were taken from the 0 to 0.3 and 0.3 to 0.6 m depths, and electromagnetic (EM) induction was also done. Although the study area was nearly level (< 0.5 m change in elevation), elevation was significantly correlated with soil variables except for Na%. In addition, dispersion, Na%, and EC were correlated which was expected since both EC and Na control a soil's ability to swell and disperse. All of the soil variables exhibited patchiness across the study area. The EM38, used to determine ECa, was determined to be highly reliable to express soil EC distribution and was correlated with Na% and dispersion. Therefore, the use of an EM38 may allow for site-specific management of Na on this low EC, nearly-level landscape. However, due to the variation encountered within the data, electronic methods should not be the sole measurement and used in place of direct soil sampling for determining the distribution and concentration of soil Na.

## Introduction

Sodic soils often have high spatial variability at the field scale and have a significant relationship with microtopography and waterlogging (Hopkins et al., 2012; Yang et al., 2011), shallow groundwater quality (Derby et al., 2013), and subsurface drainage (Moustafa and Yomota, 1998). Therefore, the non-heterogeneity of sodicity makes it difficult for site-specific management. Sodic soil quality can be reflected in crop production within fields (Corwin et al., 2003), and can be used to predict soil degradation, locate soil sampling sites, and make amendments maps (Amezqueta, 2007). An understanding about the distribution and relationship of Na and EC may be helpful in managing these problem soils.

To investigate the distribution of sodic soil properties, sodium adsorption ratio (SAR), electrical conductivity (EC<sub>e</sub>), exchangeable sodium percentage (ESP), and soil physical properties have all been used. In addition, geostatistical methods have been used to interpolate the sodic conditions (Amezqueta et al., 2007; Shouse et al., 2010). However, these measurements can be costly and labor-intensive and therefore the use of electromagnetic inductions (EM) techniques have been found to be able to successfully estimate EC distribution in saline soils which oftentimes has a close relationship to SAR (Corwin et al., 2003; Shouse et al., 2010). These measurements are most often conducted by agronomists for zone-sampling strategies but the value of the measurements can be lessened if the spacing between measurements is too great or if the soil is too dry. Furthermore, ground elevation has been shown to be an important environmental factor influencing the spatial variation of soil salinization (Gokalp et al., 2010; Yang et al., 2011), so the coupling of elevation, EM, and SAR may hold promise for predicting sodicity.

As subsurface tile drainage installation increased in the northern Great Plains, and farmers are looking for ways to improve the production potentials of sodic soils, questions exist about where to apply amendments such as gypsum and sulfur sodic-soils. Currently, one may suggest applying amendments by Natric soil-mapping units but given the variability of these sodic soils (varying degrees of severity) this may lead to unnecessary application and costs. The cost for pelletized gypsum is currently about \$218 US Mg<sup>-1</sup> (A. Hoiberg, personal communication, 2014) and synthetic gypsum is not yet available to this region.

The results from papers 2 and 3 indicate that dispersion and swelling will likely reduce the flow of soil water when the EC of the soil solution decreases through losses of water and electrical-conductive ions out of the tiles. To date, limited data exists in the northern Great Plains in connecting nearly-level land surface properties with the distribution of Na in soils classified as being Natric (Soil Survey Staff, 1999). Therefore, the objective of this study was to characterize the spatial variation of Na and its relationship to environmental (elevation and topographic wetness index) and chemical factors (EC<sub>1:1</sub>, pH<sub>1:1</sub>, %Na, ECa, and dispersion) to determine the likelihood of making site-specific amendment recommendations for effective sodic soil management.

## **Materials and Methods**

### **Site description**

The study area was 8.1 ha in size and was located in southeastern North Dakota, USA (Lat. 46.28 N, Long. 97.25 W) (Fig. 11). The soils in this area were developed from when the Sheyenne River emptied into Lake Agassiz and created the Sheyenne Delta (Bluemle, 2000). The soils in study area are Exline (Fine, smectitic, frigid, Leptic Natrudolls) and Stirum-Arveson (Stirum: Coarse-loamy, mixed, superactive, frigid, Typic Natraquolls; Arveson: Coarse-loamy,

mixed, superactive, frigid Typic Calciaquolls). The change in elevation above sea-level at the site is less than 0.5 m. The 30-yr average annual precipitation is 580 mm, annual potential evapotranspiration is about 1160 mm (North Dakota Agricultural Weather Network), and the depth to groundwater in spring within this region is often less than 0.3 m from soil surface (Baker and Paulson, 1967). Prior to use as cropland, the field was used as hayland for over 20 years, and then had subsurface tile drain installed (24.4 m spacing, about 1.2 m deep) during the fall 2012, and cropped corn (*Zea mays*) in both 2013 and 2014.

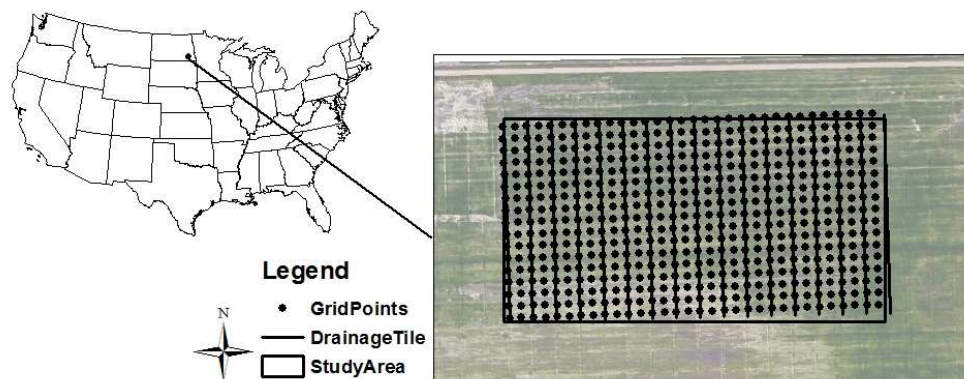


Fig. 11. Map showing the relative location of the study site and the grid sample locations (n = 544).

### Data collection and measurement

Using a 12.2 m $\times$ 12.2 m grid pattern 544 sampling sites were determined using ArcGIS (version 10.1) and the sampling sites were selected over existing tile drains and directly between drainage tiles (Fig. 11) to determine if tile installation and short-term drainage influenced soil properties. All measurements were geo-referenced with Real Time Kinetic (RTK) GPS (Model: R4 Receiver and TSC2 Data Controller, Trimble Navigation Limited, Sunnyvale, CA). Error of RTK is less than 0.01 m in horizontal and between 0.01 and 0.02 m in vertical. To determine the elevation using RTK in study area, an average distance of 2.3 m was used. After that an elevation

shape file was created and was later converted into a Digital Elevation model (DEM) raster file through a Topo to Raster function in ArcMap. The elevation of grid points (n = 544) were extracted through “extract values to points” in spatial analysis tools of ArcMap. Although LiDAR data is available for this region its resolution was not sufficient for this nearly-flat landscape.

Apparent electrical conductivity (ECa) at horizontal and vertical directions were determined at each sampling point using EM38 (Geonics, Ltd. Mississauga, ON, CA) and readings were corrected for temperature and calibrated using ECe (EC from saturated paste extract) following the procedures outlined in McKenzie et al. (1989) and Wollenhaupt et al. (1986). For calibration seven points that reflected the spatial heterogeneity of the ECa measurements were used to determine weighted ECe and then to determine ECa (Fig. 12).

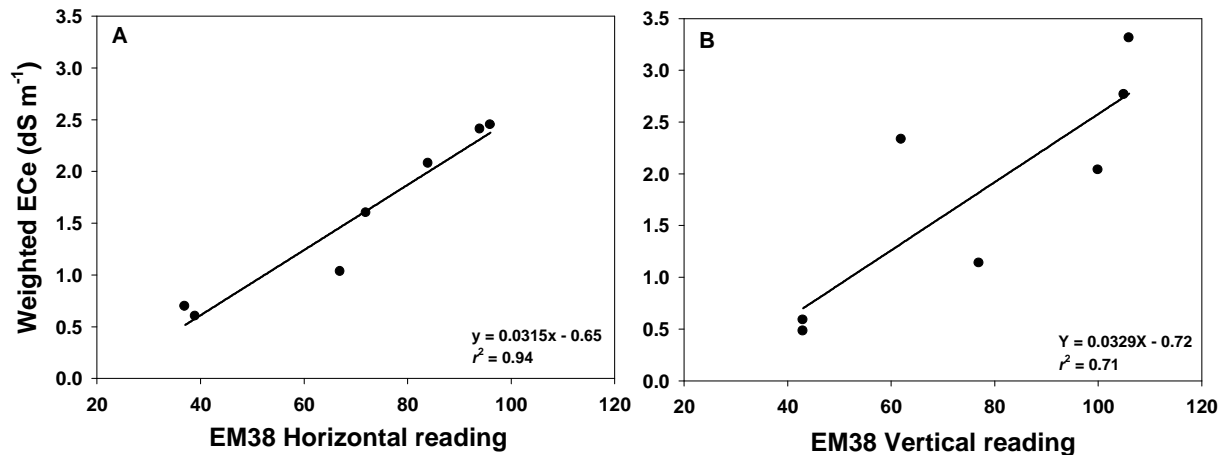


Fig. 12. Correlation of weighted profile ECe and EM38 readings taken in horizontal (A) and vertical (B) positions.

At each location, two 3.2 cm diameter soil cores were taken to a depth of 0.6 m and respective 0-0.3 m and 0.3-0.6 m depths composited into paper bags, followed by being air dried, and ground to pass through 2 mm sieve. Extraction of soluble and exchangeable phase Na was

accomplished by shaking 1 g of soil with 20 mL of 1M NH<sub>4</sub>OAc, followed by centrifugation at 647 ×g for 10 min. After centrifugation, Ca, Mg, Na, and K were quantified by atomic adsorption spectrophotometer (Model 200A, Buck Scientific). The extractable Na% was calculated as Na/(Ca + Mg + Na + K) where units of each cation were cmol<sub>c</sub> kg<sup>-1</sup>, which include both soluble and exchangeable ions and is a little bit different from ESP. Soil EC and pH were measured using a 1:1 soil slurry (U.S. Salinity Laboratory Staff, 1954).

The dispersion of soils was determined using the Crumb Test following ASTM method D 6572 (American Society for Testing and Materials, 2004) where 1.5 cm cubes of soil were prepared by hand with distilled water (DW) and gently lowered into petri dishes containing DW water. The grade of dispersion, which ranged from 1 (no dispersion) to 4 (severe dispersion) was recorded at 2 min, 1 h and 6 h. Binary categories were set as 1 = dispersion when the grade was 3 or 4 and 0 = no dispersion when the grade was 1 or 2.

### **Data statistical analysis**

Variograms are a useful method to determine the average sample variance for samples between each other taken at increasing distances (Li et al., 2009). Variograms in isotropic models were produced by GS+ 10.0 (Gamma Design Software, LLC, Plainwell, Michigan). Isotropic models were selected in the study because preliminary data showed that isotropic models had higher percentage variation explained by model than anisotropic models. A lag distance of 12.2 m was used for the semivariance analysis since the sampling design for the field was based on a 12.2 m ×12.2 m grid. Descriptive statistics were conducted for original data, however, the geostatistical analysis were based on logarithmic transformation of data to increase the normality in the study.

Interpolation of index kriging for soil dispersion data was performed based on the input of variogram in GS+10.0. The remaining spatial data were all entered into a geographic information system (GIS) using ArcMap10.1 (ESRI ArcMap 10.1, Redlands, CA). Maps of soil  $EC_{1:1}$ ,  $EC_{ah}$ ,  $EC_{av}$ ,  $pH_{1:1}$ , Na%, and elevation data were prepared by interpolating the measurements using inverse-distance-weighted (IDW) in order to aid in visualization and comparison of data in ArcMap. Different terrain variables were derived from elevation DEM, including slope, flow direction, flow accumulation, and topographic wetness index (TWI). Both flow accumulation and TWI were found to be useful to help quantify the influence of topography on soil chemical properties (Sorensen et al., 2006). Flow accumulation models were developed using elevation DEM (1 m resolution). The TWI combines local slope and flow accumulation, and has effects on hydrological processes. The TWI is defined as  $TWI = \ln(\alpha/\tan\beta)$ , where  $\alpha$  is a potential flow accumulation to a specific location,  $\tan\beta$  indicates the local drainage potential (Beven and Kirkby, 1979). Finally, Pearson correlation coefficients ( $r$ ) were calculated for all pairs of variables ( $EC_{1:1}$ ,  $pH_{1:1}$ , ECa horizontal ( $EC_{ah}$ ), ECa vertical ( $EC_{av}$ ), Na%, dispersion, elevation, and TWI) to determine the strength of relationships. In  $r$  calculation, elevation and TWI were originally raster based, so they were extracted to grid points for their value at each grid point. Environmental factors for this study were elevation, TWI and the remaining soil variables were  $EC_{1:1}$ ,  $pH_{1:1}$ , ECa horizontal ( $EC_{ah}$ ), ECa vertical ( $EC_{av}$ ), Na%, and dispersion.

## **Results and Discussion**

### **Environmental factors**

The elevation of the study site changed less than 0.5 m with a slope of less than 0.8%, indicating the study area was very flat. Overall, one long and two short flow accumulation networks were observed in the field in the northwest corner and southeast corner and they had



higher number of pixels in high flow accumulation categories than the rest of study area (Fig. 13). The network indicated in which direction the outflow from a given cell will be distributed to the neighboring downslope cells (Rampi et al., 2014). Correspondingly, TWI also indicated that there were a few spots in the south and northeastern corners of study area that displayed higher TWI values, probably influencing the following patterns of the soil chemical variables (Fig. 13).

Among many terrain variables, TWI is a factor that considers both field slope and flow accumulation, and is considered to be a good indicator of soil moisture distributions at different landscape positions (Pei et al., 2010). In addition, TWI was found to be effective at predicting soil organic matter distribution (Pei et al., 2010), soil water content (Barling et al., 1994), and locating wetland locations with other ancillary data (Rampi et al., 2014). Compared to other studies, the TWI in our study site was small. However, exception occurs in the middle of study area where a line going across west to east was not a natural feature and was probably caused by historical surface drainage.

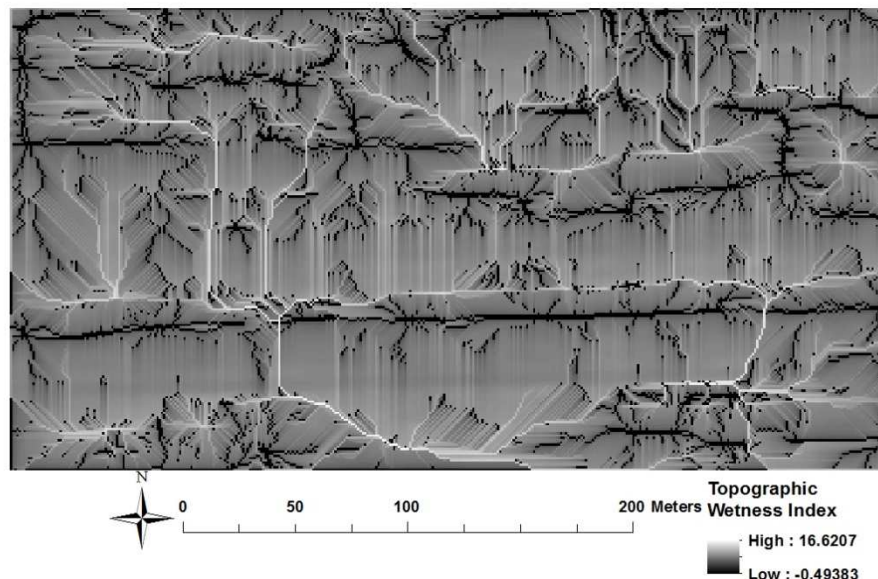


Fig. 13. The topographic wetness index (TWI) of the study area in field.

## **Spatial analysis**

The extent of spatial dependence is expressed as the proportion  $(C/(C_0+C))$  (Table 10) (Rodriguez et al., 2009) where the value lies between 0 and 1 and values close to 1 indicate spatial dependence inherent in the dataset while a value of 0 indicates no spatial dependence through the data range. The extent of spatial dependence of the soil variables specified in our study ranged from 0.501 to 0.878 and from 0.503 to 0.885 in 0 to 0.3 and 0.3 to 0.6 m, respectively (Table 10). The range values represent the distance at which the asymptote is reached, and when the distance is beyond this range the samples are independent (Ettema and Wardle, 2002). The range distances in our study were much greater than the lag distance 12.2 m (Table 10) which indicates that our sampling design was appropriate and can accurately detect variations within the soil variables. These statistical results indicated that the IDW and kriging are reliable interpolations across the distances because we are not attempting to interpolate outside the effective range in our field (Ettema and Wardle, 2002).

## **Soil chemical factors**

Across the study site the EC<sub>a</sub> was less than 3 dS m<sup>-1</sup> from both soil depths but there was a trend of EC to increase with depth (Fig. 14). However, EC<sub>1:1</sub> values were mostly less than 1 dS m<sup>-1</sup> (Fig. 15) which can be expected since saturated-paste derived EC is about two times greater than the EC of a 1:1 diluted sample (Sonmez et al., 2008). Irrespective of the EC approach, similarity between Fig. 14 and 15 exists which can be represented by the comparative  $r$  value near 0.60 between them (Table 11). The pattern of EC can be attributed to microtopography (Derby et al., 2013) where in our study site the higher values of EC were found on lower depression areas located in areas of high water accumulation and TWI, where salts accumulate

after evaporation. This was also in agreement with the results from Douaik et al. (2005) in that the elevation was a major factor influencing soil salinization.

Table 10. Descriptive statistics and geostatistical summary of soil factors. Geostatistical analysis was conducted on log-transformed data.

Statistic	EC <sub>1:1</sub>	pH <sub>1:1</sub>	Na%	Dispersion	ECav <sup>†</sup>	ECah <sup>‡</sup>
-----0 to 0.3 m-----						
Model <sup>§</sup>	Spherical	Spherical	Exponential	Exponential	Spherical	Spherical
Sill (C <sub>0</sub> +C) <sup>§</sup>	0.044	0.001	0.629	0.011	0.066	0.010
Nugget (C <sub>0</sub> ) <sup>§</sup>	0.022	0.0004	0.077	0.001	0.014	0.003
Proportion (C/[C <sub>0</sub> +C]) <sup>§</sup>	0.501	0.577	0.878	0.872	0.779	0.708
Range <sup>§</sup>	82.40	126.7	72.00	48.6	76.80	75.40
r <sup>2</sup> <sup>§</sup>	0.877	0.951	0.967	0.481	0.985	0.977
Mean <sup>¶</sup>	0.451	8.454	1.871	-	1.419	1.209
Minimum <sup>¶</sup>	0.236	7.68	0.151	-	0.469	0.516
Maximum <sup>¶</sup>	0.947	9.77	14.07	-	2.772	2.374
SD <sup>¶</sup>	0.103	0.287	1.744	-	0.37	0.328
Skewness <sup>¶</sup>	1.410	0.720	2.990	-	0.910	0.650
Kurtosis <sup>¶</sup>	3.790	1.550	13.05	-	0.990	2.140
-----0.3 to 0.6 m-----						
Model	Spherical	Exponential	Exponential	Exponential	Spherical	Spherical
Sill (C <sub>0</sub> +C)	0.157	0.001	0.645	0.019	0.066	0.01
Nugget (C <sub>0</sub> )	0.078	0.0001	0.074	0.002	0.015	0.003
Proportion (C/[C <sub>0</sub> +C])	0.503	0.884	0.885	0.875	0.779	0.708
Range	97.30	47.10	50.10	37.50	76.80	75.40
r <sup>2</sup>	0.882	0.909	0.929	0.751	0.985	0.977
Mean	0.420	8.975	2.772	-	1.419	1.209
Minimum	0.168	7.47	0.162	-	0.469	0.516
Maximum	2.680	9.89	15.78	-	2.772	2.374
SD	0.242	0.362	2.236	-	0.370	0.328
Skewness	4.160	-0.550	2.060	-	0.910	0.650
Kurtosis	25.64	1.120	6.250	-	0.990	2.140

† ECav, ECa in vertical direction.

‡ ECah, ECa in horizontal direction.

§ Geostatistics.

¶ Descriptive statistics, where SD is standard deviation.

Variations of Na% were quite small in the upper soil profile, indicating considerable field uniformity to a depth of about 0.3 m (Table 10). With depth, however, the average Na% increased at 0.3 to 0.6 m and was distributed in patches (Fig. 16). Relatively higher Na% was observed in the corners while lower Na% was located in the middle of the study area. The Na% values above 10% were mainly found in the southern portion of the study area. High Na% may have resulted in a rise of pH, and their respective distributions were consistent ( $r \approx 0.6$ ) (Fig. 16). About 90% of the 0.3 to 0.6 m depth had pH values greater than 8.6, likely explained by the hydrolysis effect of Na (Guerrero-Alves et al., 2002).

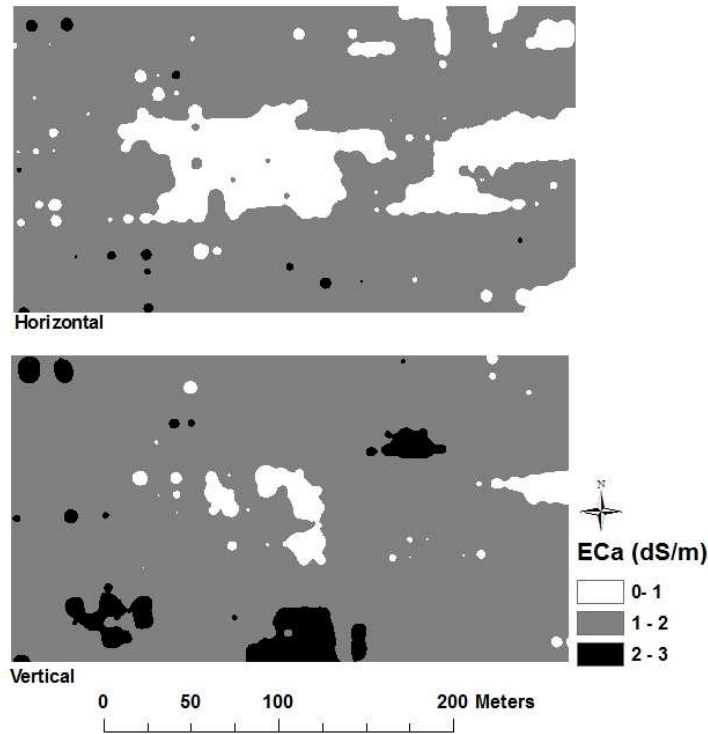


Fig. 14. Inverse distance weighted interpolated maps of ECa at 544 sites.

The patchiness of the study area was likely due to variable textures due to slight changes in elevation, which would drive capillary water movement from groundwater (Shouse et al., 2010). However, no significant correlation was found between Na% and elevation, probably

because Na in our study was mainly from the soil exchange sites instead of in the soluble phase. The shallowest water table in this region is about less than 0.3 m below the surface during spring thaw (Baker and Paulson, 1967). The North Dakota Geological Survey in 1967 reported that the groundwater of Dakota sandstone aquifer had a Na concentration of 1,010 ppm in the Township 132 N and Range 52 W, near where the study area was located (Baker and Paulson, 1967). Therefore, groundwater is the likely source of Na to the soils in this region and can be accentuated by low precipitation and high evaporation (NDAWN). Even though the TWI was not significantly related with Na% (Table 11), the four estimated water accumulation locations in Fig. 16 showed high Na% patches with values ranging from 10 to 16%. Support of this finding was also noted by Derby et al (2013) where high soil Na and EC were linked to depressional areas near Oakes, North Dakota.

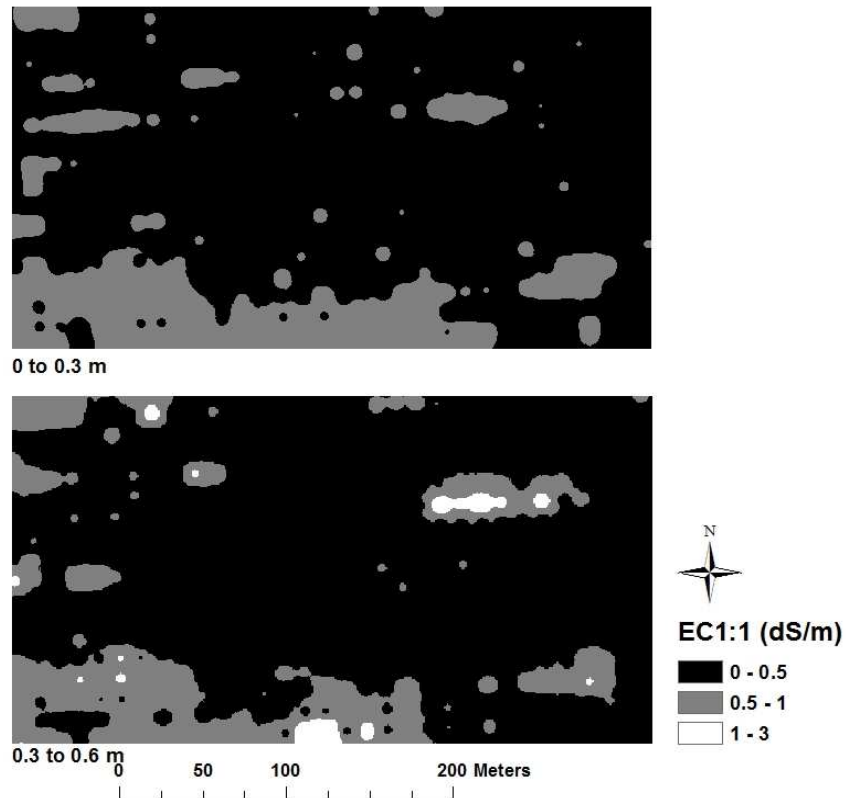


Fig. 15. Inverse distance weighted interpolated maps of EC<sub>1:1</sub> at 544 sites.

## Dispersion

Dispersion was evident for about one-half of the samples and also displayed heterogeneity for both soil depths (Fig. 17). There were many patches and sharp discontinuities reflecting “hot” and “cold” spots, and this pattern was similarly described by Ettema and Wardle (2002). About 30% of soils showed dispersion in the surface 0 to 0.3 m of the field whereas more than 60% of soils in 0.3 to 0.6 m depth showed dispersion. Notable, dispersion was observed even in areas with Na values around 5%.

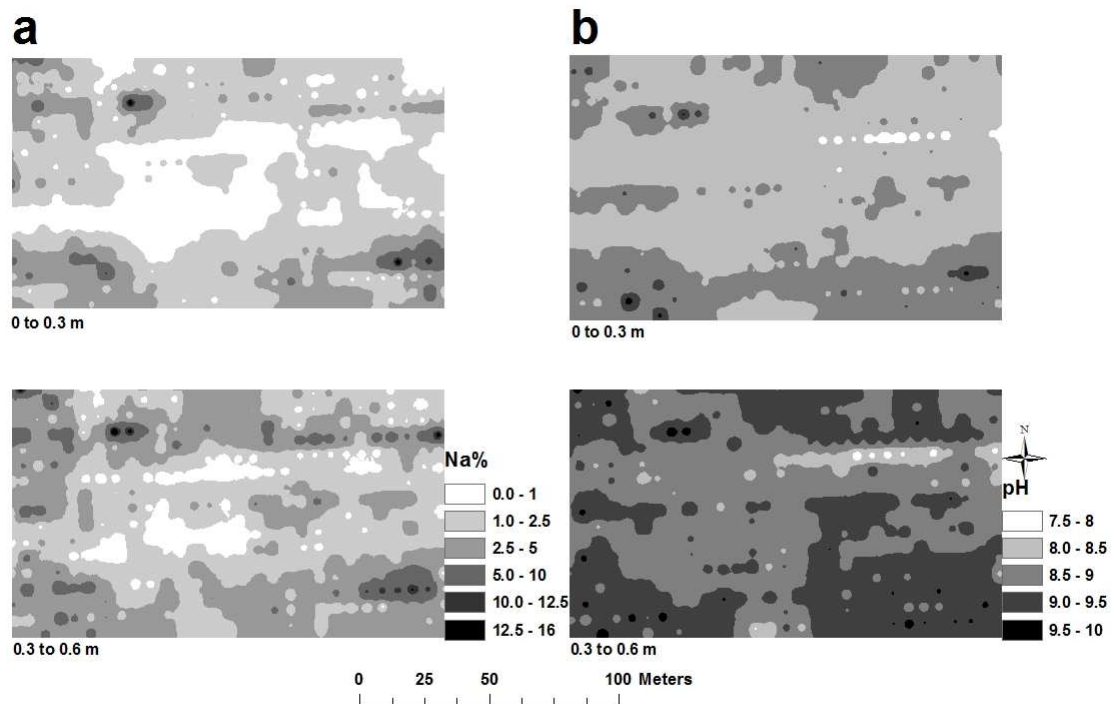


Fig. 16. Inverse distance weighted interpolated maps of Na% and pH, a: Na%, and b: pH at two depths of 544 sites.

Dispersion was influenced by interactive factors of Na and EC (Essington, 2004; He et al., 2013; Quirk and Schofield, 1955). Therefore, the pattern of dispersion in the study field should be related with Na% and EC. The EC values were less than  $3 \text{ dS m}^{-1}$  all across the field, probably not meeting the field flocculation value which was defined by Amezketa et al. (2003)

as the minimum electrolyte concentration required to prevent soil dispersion at a given SAR. The Na% should be a limiting factor affecting sodic soil dispersion and in this study the Na% was found to be highly correlated with dispersion ( $r = 0.67$ ) for both depths (Table 11).

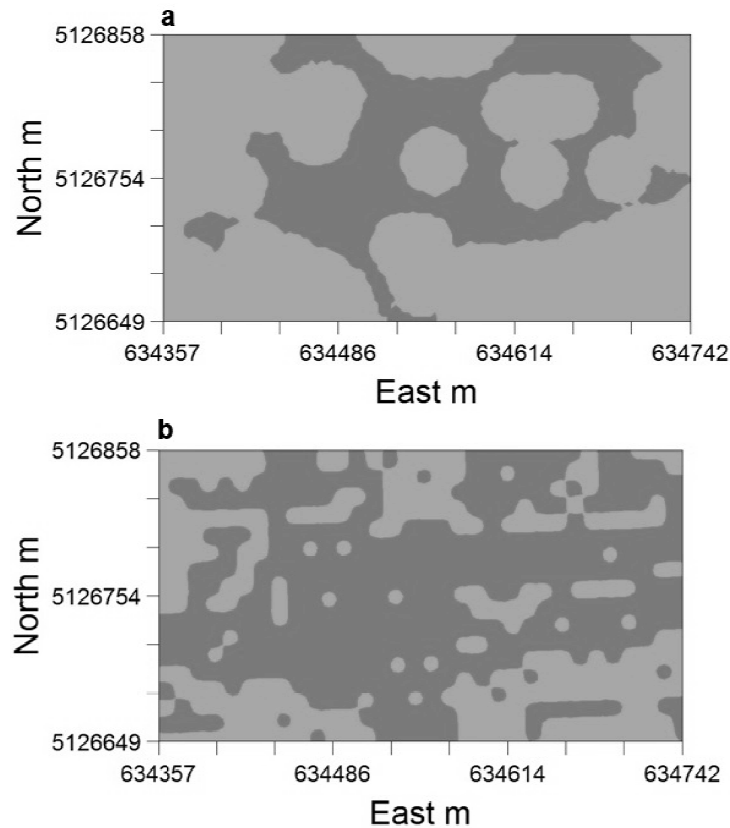


Fig. 17. Index kriging maps of dispersion for 544 sites at two depths, a: 0 to 0.3 m, b: 0.3 to 0.6 m, the lighter grey pattern color indicates no dispersion.

### Targeted sodic soil management

As hypothesized, the soil parameters EC, Na%, pH, and dispersion varied aerially and with depth across the study area and sampling location (over the tile vs. between the tiles) was not considered to be a confounding variable (Appendix Table C1). For example, low Na% soils were interspersed by high Na% soils (Fig. 16) and EC measurements were significantly correlated with elevation, in addition to dispersion and pH (Table 11). Unfortunately, aerial photos taken during the growing season (Appendix: Fig. C1 and C2) were not able to predict

Na% (Greenness index was calculated, data not shown), but non-uniform crop greenness was undoubtedly related to soil and environmental factors, which was supported by Sorensen et al. (2006) in that 52% of variation in plant richness was related with TWI. Although Na% and elevation were not correlated, Na% was highly correlated with EC<sub>1:1</sub> and the EM38 EC readings, which gives promise to being able to predict where sodic soil amendments could be directed.

Table 11. Pearson correlation (*r*) of all data (n= 544) in the study area.

Parameters	Elevation	TWI <sup>†</sup>	EC <sub>1:1</sub>	pH <sub>1:1</sub>	Na%	Dispersion	ECav	ECah
-----0 to 0.3 m-----								
Elevation	1.00	-0.23 <sup>*</sup>	-0.35 <sup>*</sup>	-0.20 <sup>*</sup>	-0.06	-0.15 <sup>*</sup>	-0.32 <sup>*</sup>	-0.34 <sup>*</sup>
TWI	-0.23 <sup>*</sup>	1.00	0.06	0.04	0.05	-0.003	0.08 <sup>*</sup>	0.09 <sup>*</sup>
EC <sub>1:1</sub>	-0.35 <sup>*</sup>	0.06	1.00	0.29 <sup>*</sup>	0.54 <sup>*</sup>	0.40 <sup>*</sup>	0.58 <sup>*</sup>	0.64 <sup>*</sup>
pH <sub>1:1</sub>	-0.21 <sup>*</sup>	0.04	0.29 <sup>*</sup>	1.00	0.68 <sup>*</sup>	0.55 <sup>*</sup>	0.40 <sup>*</sup>	0.48 <sup>*</sup>
Na%	-0.06	0.05	0.54 <sup>*</sup>	0.68 <sup>*</sup>	1.00	0.68 <sup>*</sup>	0.49 <sup>*</sup>	0.57 <sup>*</sup>
ECav <sup>‡</sup>	-0.32 <sup>*</sup>	0.08 <sup>*</sup>	0.58 <sup>*</sup>	0.40 <sup>*</sup>	0.49 <sup>*</sup>	0.34 <sup>*</sup>	1.00	0.89 <sup>*</sup>
ECah <sup>§</sup>	-0.34 <sup>*</sup> ¶	0.09 <sup>*</sup>	0.64 <sup>*</sup>	0.48 <sup>*</sup>	0.57 <sup>*</sup>	0.40 <sup>*</sup>	0.89 <sup>*</sup>	1.00
Dispersion	-0.15 <sup>*</sup>	0.00	0.40 <sup>*</sup>	0.55 <sup>*</sup>	0.68 <sup>*</sup>	1.00	0.34 <sup>*</sup>	0.40 <sup>*</sup>
-----0.3 to 0.6 m-----								
Elevation	1.00	-0.23 <sup>*</sup>	-0.21 <sup>*</sup>	-0.04	0.07	0.01	-0.32 <sup>*</sup>	-0.34 <sup>*</sup>
TWI	-0.23 <sup>*</sup>	1.00	0.02	-0.02	-0.01	-0.02	0.08 <sup>*</sup>	0.09 <sup>*</sup>
EC <sub>1:1</sub>	-0.21 <sup>*</sup>	0.02	1.00	0.02	0.43 <sup>*</sup>	0.27 <sup>*</sup>	0.64 <sup>*</sup>	0.62 <sup>*</sup>
pH <sub>1:1</sub>	-0.04	-0.02	0.02	1.00	0.64 <sup>*</sup>	0.63 <sup>*</sup>	0.28 <sup>*</sup>	0.34 <sup>*</sup>
Na%	0.07	-0.01	0.43 <sup>*</sup>	0.64 <sup>*</sup>	1.00	0.67 <sup>*</sup>	0.52 <sup>*</sup>	0.57 <sup>*</sup>
ECav	-0.32 <sup>*</sup>	0.08 <sup>*</sup>	0.64 <sup>*</sup>	0.28 <sup>*</sup>	0.51 <sup>*</sup>	0.37 <sup>*</sup>	1.00	0.89 <sup>*</sup>
ECah	-0.34 <sup>*</sup>	0.09 <sup>*</sup>	0.62 <sup>*</sup>	0.34 <sup>*</sup>	0.57 <sup>*</sup>	0.39 <sup>*</sup>	0.89 <sup>*</sup>	1.00
Dispersion	0.01	-0.02	0.27 <sup>*</sup>	0.62 <sup>*</sup>	0.67 <sup>*</sup>	1.00	0.37 <sup>*</sup>	0.39 <sup>*</sup>

† TWI, Topographic wetness index.

‡ ECav, ECa in vertical direction.

§ ECah, ECa in horizontal direction.

¶ Significant at 95% of confidence interval.



Nearly-level landscapes, such as what is found in the Red River Valley of the North Dakota, an alluvial landscape developed about 9,000 yr ago, pose a challenge to predicting soil properties based on elevation changes. LiDAR has been a common tool to look at watershed water-flow modeling but this elevation tool fails at the smaller landscape scales (hectares) due to surface vegetation and obstacles (e.g. cattle, hay bales, weeds) and the attempt to interpret elevation changes within the study area using LiDAR for this study failed. The use of RTK, however, coupled with TWI modeling may be practical approach for determining soil EC which can then be used for modeling Na%.

Spatial variability influences the size and number of soil samples required to characterize the properties in an area of interest (Corwin et al., 2003). Therefore, the spatial variability displayed in Table 10 indicated that a grid distance of 12.2 m was effective in determining samples for Na% levels. Given that the location of the tiles did not influence the variables, a 24 m distance was also acceptable but may yet not be practical for routine soil sampling. In very flat areas without influence of TWI, the sampling distance can be greater than 24 m, similar to results found in Franzen et al. (2002) where a grid (33 or 66 m) or topographic approach could be correlated with Order 1 survey-based sampling for N-management. Therefore, the sampling number could be decreased to about 200 or less in our study area.

When high Na exists soil dispersion and or swelling will occur which can affect the spatial variation of soil water potentials (Gokalp et al., 2010). Therefore, Na may cause soils to adsorb water more than their liquid limit and remain wetter longer (Grim, 1968), which is supported by Paper 3 that field capacity water was greatly increased due to high Na and low EC. The study in Paper 3 found that an SAR of greater than 5 could cause an increase of field capacity water and a swelling increase as little as 16 to 25% can decrease saturated hydraulic

conductivity to one third of its original value (Curtin et al.,1994; Shabtai et al., 2014). In an unpublished study Na% was significantly related with SAR ( $SAR = 1.04 \text{ Na\%} - 0.35$ ,  $r^2 = 0.92$ ) (DeSutter, unpublished data, 2014) and therefore it is reasonable to use Na% in place of SAR to predict soil-water relations and therefore a Na% of 5 corresponds to an SAR of 5.

Using the information from this study and a target Na% of 5 or less, gypsum rates and costs can be determined for site-specific management. Considering only the 0-0.3 m depths, 24 of the 544 sample locations require gypsum. For this situation each sample location (12.2 x 12.2 m) would require between 0 and 0.64 Mg (0 and 0.7 tons). Using the estimate for gypsum of  $\$218 \text{ Mg}^{-1}$  ( $\$240 \text{ ton}^{-1}$ ), the cost for gypsum for this 8.1 ha, considering only the 0-0.3 m depth, would be about \$1,100 (US) which include the recommended 25% increase in application rate to account for lack of 100% efficiency (U.S. Salinity Laboratory Staff, 1954). For the 0.3-0.6 m depth, which largely had Na% greater than 5%, costs can significantly increase if complete remediation is the objective. See Appendix D for example calculations.

### **Conclusions**

In this nearly-level landscape high spatial variability was observed for soil Na, EC, pH, and dispersion. The Na% and EC were found to be effective for estimating dispersion zones and EM38 for estimating soil EC. Except for Na% the environmental factor elevation was related with all other soil variables and can be used to target sampling sites within problem areas. Therefore, on this nearly-level landscape one could use EM38 or other apparent electrical conductivity sensor and elevation (RTK) for determination of areas that may likely be sodic but soil sampling should also be done to verify modeled data.

## Acknowledgments

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## GENERAL CONCLUSIONS

Experiments showed that soil EC and SAR were two important factors influencing sodic soil dispersion and swelling. Both processes increased as SAR increased and as EC decreased. The Ca/Mg ratios of solution did not influence clay dispersion. Dispersion occurred more in soils or clays dominated by smectite, and swelling (FCW) was also related with soil clay mineralogy. Maintaining an EC level above  $4 \text{ dS m}^{-1}$  may prevent dispersion and swelling when SAR is above 5. In addition, if tile drainage removes soluble salts from those soils that have an SAR greater than 5, the FCW may increase and thus decrease the rate of water movement. Long-term management plans for these high-risk soils should include chemical amendments. However, high spatial variability was observed for soil Na%, EC, pH, and dispersion in a nearly-level landscape but the Na% and EC were found to be effective for estimating dispersion zones. Except for Na% the environmental factor elevation was related with all other soil variables. The EM38 was determined to be highly reliable to express soil EC distribution and was correlated with Na% and dispersion. Therefore, the use of an EM38 and elevation may allow for targeting sampling sites within problem areas and for site-specific management of Na soils in nearly-level landscapes.



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**APPENDIX A. THE GYPSUM REQUIREMENT TO REPLACE EXCHANGEABLE  
SODIUM: EXAMPLE CALCULATION**

1 acre furrow slice (1 acre of top soil 6 inch) =  $2 \times 10^6$  lbs; 1 ha furrow slice (hfs) =  $2.25 \times 10^6$  kg

Ca percentage in gypsum =  $40/172 = 23.3\%$

1 meq (100 g)<sup>-1</sup> = 1 cmol<sub>(+)</sub> kg<sup>-1</sup>

Assumption: If 1 meq (100 g)<sup>-1</sup> of exchangeable Na on soil exchange site is required to be replaced by Ca from gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O).

Step 1: Total charge: the meq 100g<sup>-1</sup> (cmol<sub>(+)</sub> kg<sup>-1</sup>) in 1 ha furrow slice of soil is needed to be replaced.

$$\left(\frac{2.25 \times 10^6 \text{ kg}}{\text{hfs}}\right) * \left(\frac{1 \text{ cmol}_{(+)}}{\text{kg}}\right) = 2.25 \times 10^6 \text{ cmol}_{(+)} \text{ hfs}^{-1}$$

Step 2: The amount of Ca required to replace the total charge in Step 1.

$$\left(\frac{2.25 \times 10^6 * \text{cmol}_{(+)}}{\text{hfs}}\right) * \left(\frac{1 \text{ Eq}}{100 \text{ cmol}_{(+)}}\right) * \left(\frac{1 \text{ mol}}{2 \text{ Eq}}\right) * \left(\frac{40 \text{ g}}{\text{mol}}\right) * \left(\frac{1 \text{ kg}}{1000 \text{ g}}\right) = 450 \text{ kg Ca hfs}^{-1}$$

Step 3: The amount of gypsum that can provide the Ca required in Step 2.

$$\left(\frac{450 \text{ kg Ca}}{\text{hfs}}\right) * \left(\frac{\text{kg gypsum}}{0.233 \text{ kg Ca}}\right) = 1931 \text{ kg gypsum hfs}^{-1}$$

Step 4: Convert the amount of gypsum in Step 3 into tons gypsum/(acre foot slice).

$$\left(\frac{1931 \text{ kg gypsum}}{\text{hfs}}\right) * \left(\frac{2.2 \text{ lbs}}{\text{kg}}\right) * \left(\frac{\text{tons gypsum}}{2000 \text{ lbs gypsum}}\right) * \left(\frac{1 \text{ ha}}{2.47 \text{ acre}}\right) = 0.86 \text{ tons (acre fs)}^{-1}$$

Step 5: Convert tons (acre foot slice)<sup>-1</sup> to tons (acre foot)<sup>-1</sup>, the final value and unit is the same as that provided in the Table “6” of U.S. Salinity Laboratory Staff (1954).

$$\frac{0.86 \text{ tons}}{\text{acre fs}} * 2 = 1.7 \text{ tons (acre foot)}^{-1}$$

Step 6: Convert all units to scientific units

$$\left(\frac{1.7 \text{ tons}}{\text{acre foot}}\right) * \left(\frac{0.907 \text{ Mg}}{\text{tons}}\right) * \left(\frac{\text{acre}}{0.405 \text{ ha}}\right) * \left(\frac{\text{foot}}{0.304 \text{ m}}\right) = 12.5 \text{ Mg (ha m)}^{-1}$$

## APPENDIX B. THE MINERALOGY ANALYSIS OF SOILS USED IN PAPER 3

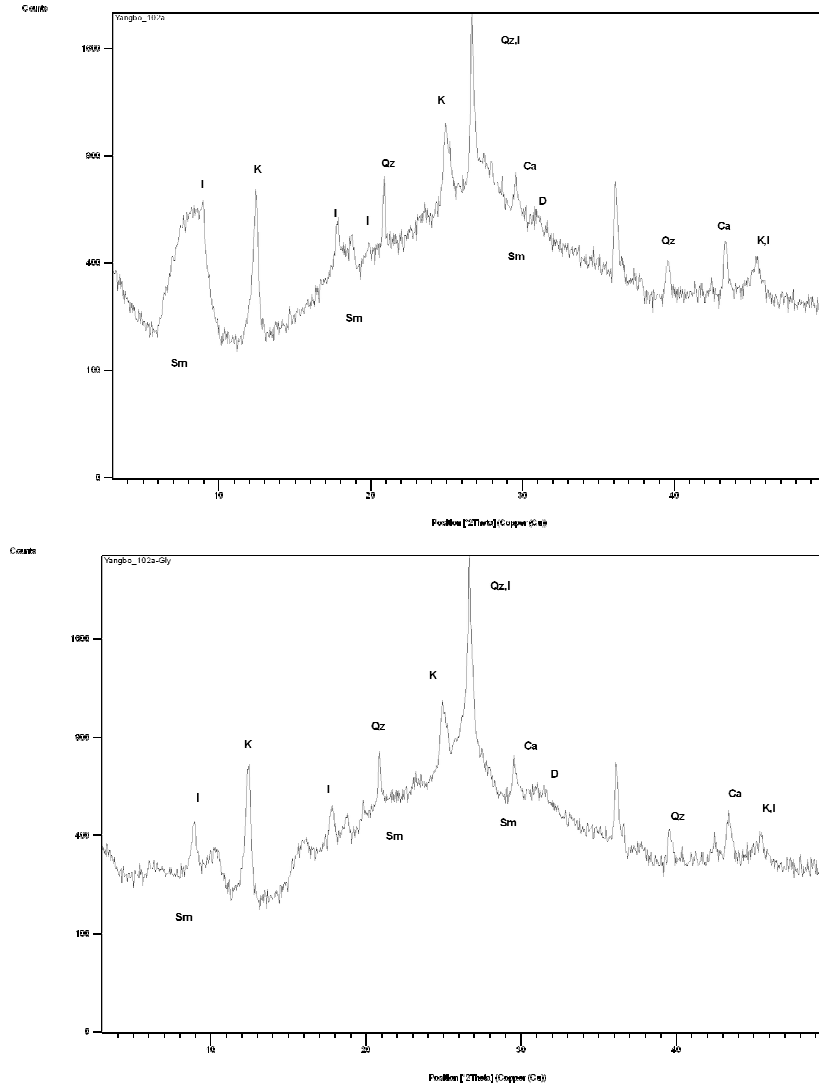


Fig. B1. The X-Ray diffraction results of Exline soil for air died sample (top) and glycolated sample (bottom).

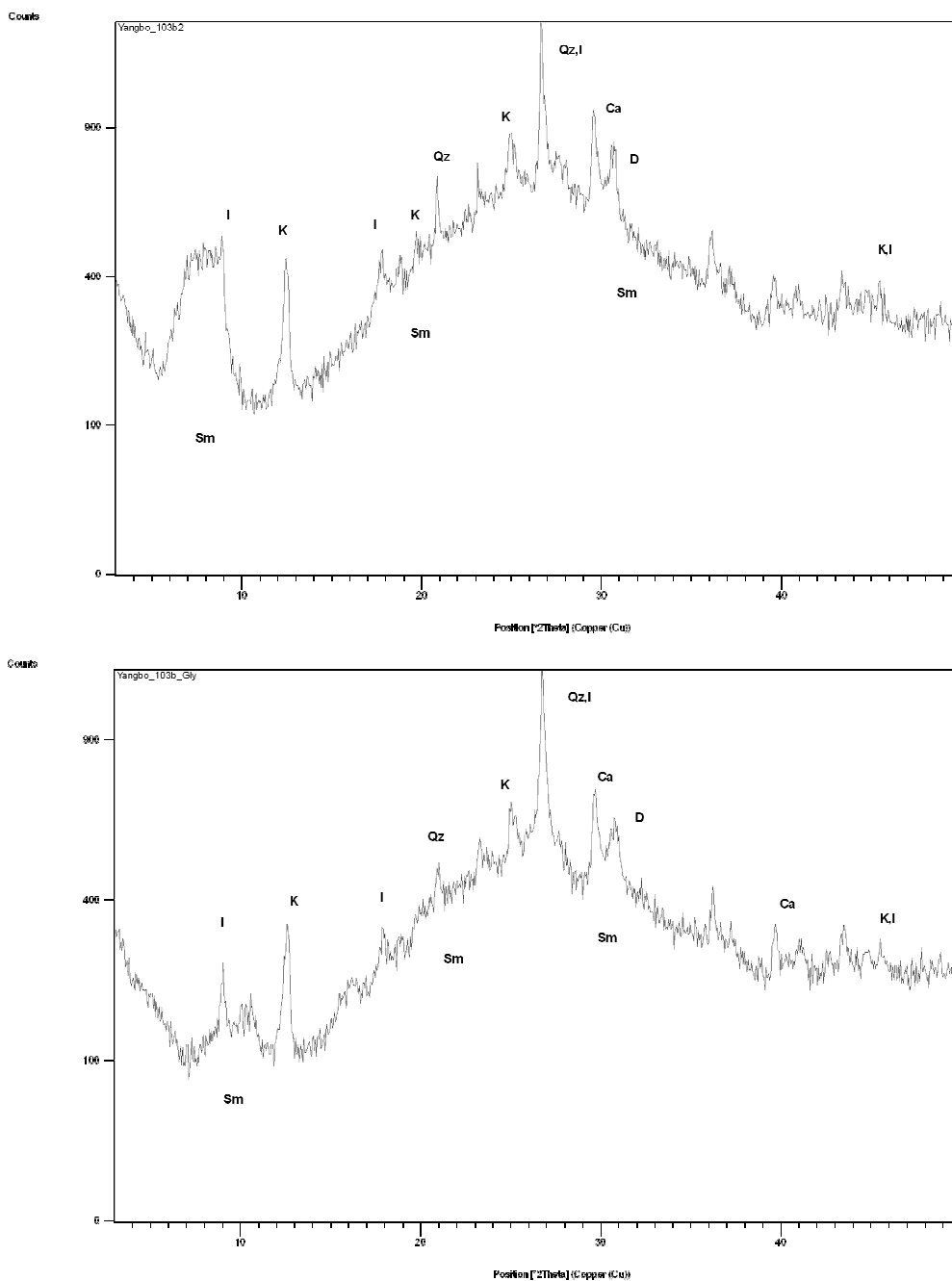


Fig. B2. The X-Ray diffraction results of Stirum soil for air died sample (top) and glycolated sample (bottom).

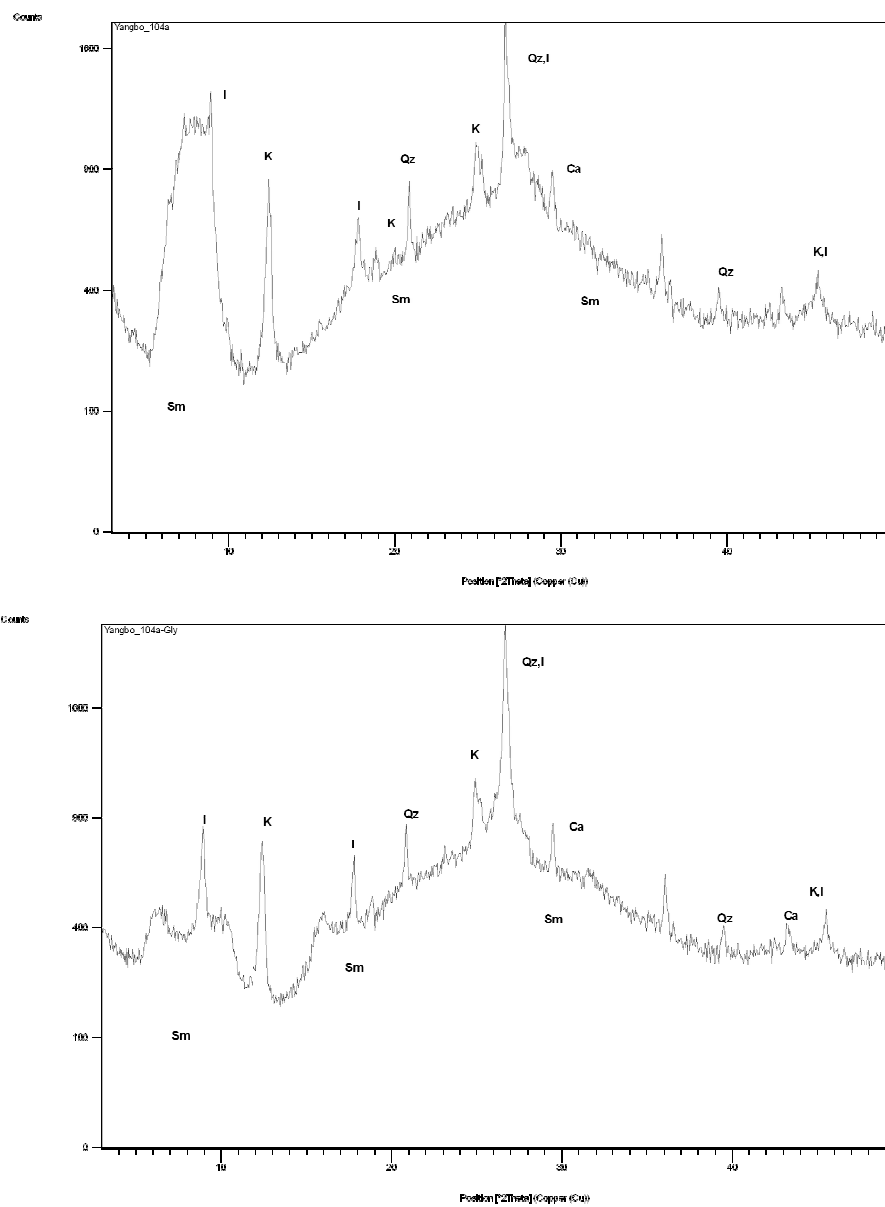


Fig. B3. The X-Ray diffraction results of Ryan soil for air died sample (top) and glycolated sample (bottom).

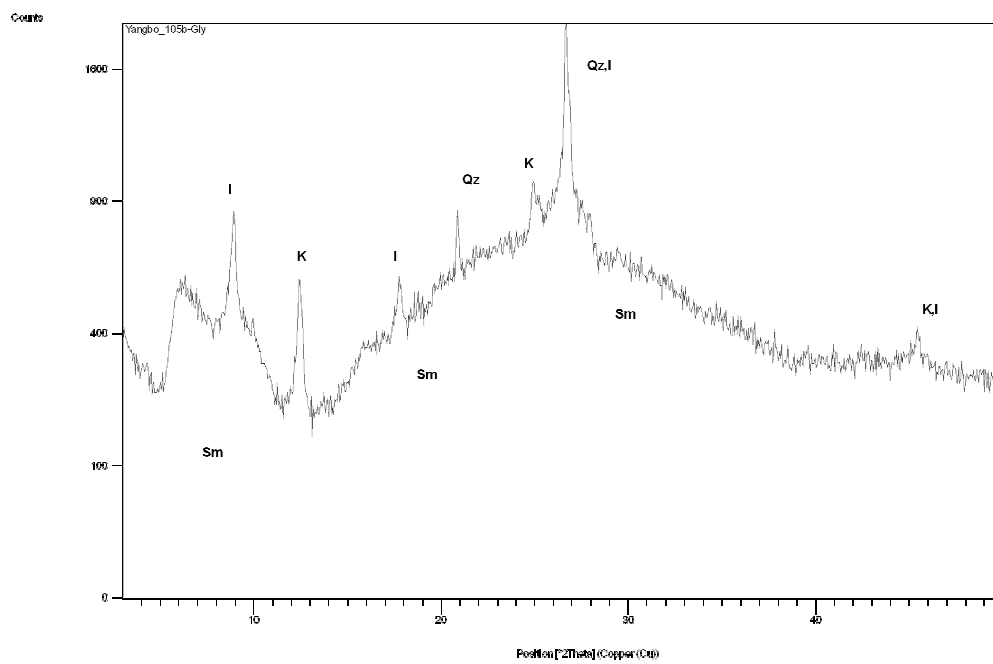
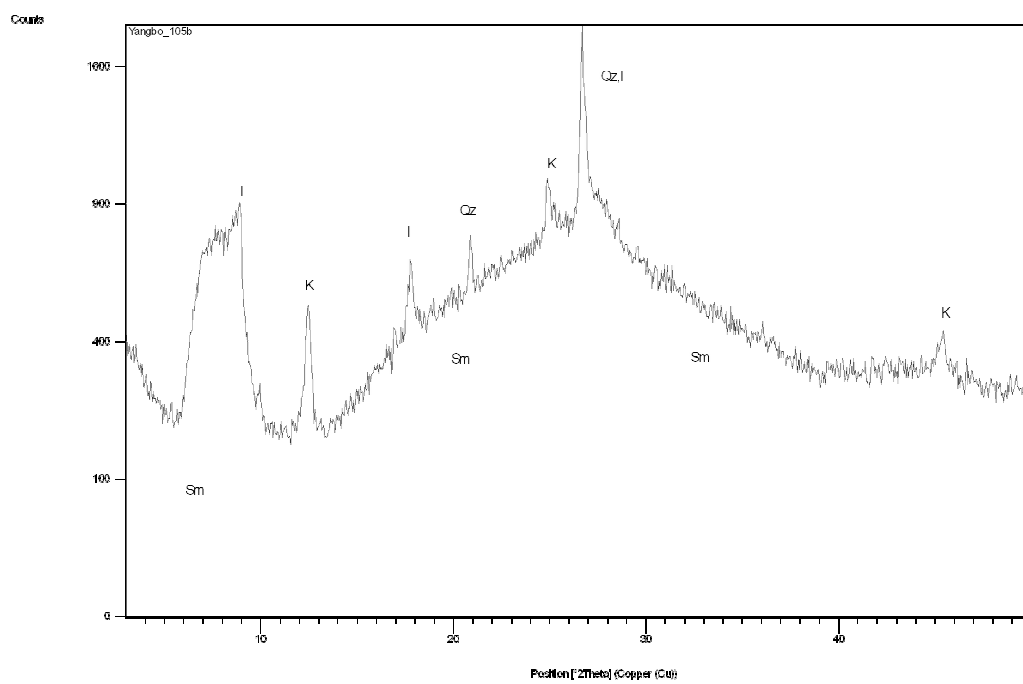
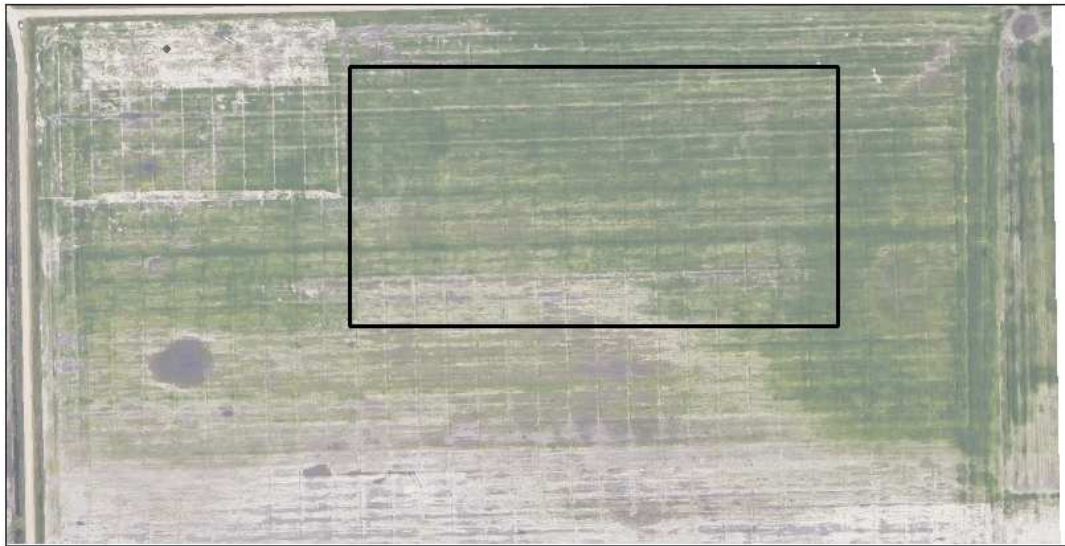


Fig. B4. The X-Ray diffraction results of Bearden soil for air died sample (top) and glycolated sample (bottom).

**APPENDIX C. THE EXPERIMENTAL DATA FOR FIELD STUDY OF PAPER 4**



**Legend**

 StudyArea

Fig. C1. The aerial photo of the research field with study area in 2013.



**Legend**

 StudyArea

Fig. C2. The aerial photo of the research field with study area in 2014.

Table C1. Pearson correlation ( $r$ ) of all data on drainage tiles and between drainage tiles in the study area for two depths 0 to 0.3 and 0.3 to 0.6 m.

Parameters	Elevation	TWI <sup>†</sup>	EC <sub>1:1</sub>	pH <sub>1:1</sub>	Na%	ECav	ECah	Dispersion
-----0 to 0.3 m on drainage tiles-----								
Elevation	1.00	-0.26*	-0.36*	-0.21*	-0.08	-0.36*	-0.36*	-0.15*
TWI	-0.26*	1.00	0.09	0.03	0.08	0.11	0.11	0.07
EC <sub>1:1</sub>	-0.36*	0.09	1.00	0.22*	0.53*	0.50*	0.60*	0.35*
pH <sub>1:1</sub>	-0.21*	0.03	0.22*	1.00	0.67*	0.32*	0.45*	0.47*
Na%	-0.08	0.08	0.53*	0.67*	1.00	0.39*	0.51*	0.65*
ECav <sup>‡</sup>	-0.36*	0.11	0.50*	0.32*	0.39*	1.00	0.88*	0.26*
ECah <sup>§</sup>	-0.36*¶	0.11	0.60*	0.45*	0.51*	0.88*	1.00	0.36*
Dispersion	-0.15*	0.07	0.35*	0.47*	0.65*	0.26*	0.36*	1.00
-----0 to 0.3 m between drainage tiles-----								
Elevation	1.00	-0.19*	-0.33*	-0.22*	-0.04*	-0.30*	-0.32*	-0.15*
TWI	-0.19*	1.00	0.02	0.04	0.01	0.06	0.07	-0.07
EC <sub>1:1</sub>	-0.33*	0.02	1.00	0.35*	0.55*	0.65*	0.68*	0.45*
pH <sub>1:1</sub>	-0.22*	0.04	0.35*	1.00	0.70*	0.46*	0.50*	0.61*
Na%	-0.04	0.005	0.55*	0.70*	1.00	0.58*	0.62*	0.71*
ECav	-0.30*	0.06	0.65*	0.46*	0.58*	1.00	0.89*	0.40*
ECah	-0.32*	0.07	0.68*	0.50*	0.62*	0.89*	1.00	0.43*
Dispersion	-0.15*	-0.07	0.45*	0.61*	0.71*	0.40*	0.43*	1.00
-----0.3 to 0.6 m on drainage tiles-----								
Elevation	1.00	-0.26*	-0.22*	-0.04	0.06	-0.36*	-0.36*	-0.04*
TWI	-0.26*	1.00	0.04	-0.01	0.03	0.11	0.11	0.04
EC <sub>1:1</sub>	-0.22*	0.04	1.00	0.07	0.44*	0.62*	0.62*	0.29*
pH <sub>1:1</sub>	-0.04	-0.008	0.07	1.00	0.65*	0.25*	0.38*	0.63*
Na%	0.06	0.03	0.44*	0.65*	1.00	0.43*	0.53*	0.66*
ECav	-0.36*	0.11	0.62*	0.25*	0.43*	1.00	0.88*	0.33*
ECah	-0.36*	0.11	0.62*	0.38*	0.53*	0.88*	1.00	0.40*
Dispersion	-0.04	0.04	0.29*	0.63*	0.66*	0.33*	0.40*	1.00
-----0.3 to 0.6 m between drainage tiles-----								
Elevation	1.00	-0.14*	-0.26*	-0.13*	-0.02*	-0.37*	-0.39*	-0.02
TWI	-0.14*	1.00	0.01	-0.03	-0.04	0.06	0.07	-0.08
EC <sub>1:1</sub>	-0.26*	0.008	1.00	-0.01	0.43*	0.66*	0.62*	0.25*
pH <sub>1:1</sub>	-0.13*	-0.03	-0.01	1.00	0.62*	0.30*	0.30*	0.62*
Na%	-0.02	-0.04	0.43*	0.62*	1.00	0.58*	0.59*	0.69*
ECav	-0.37*	0.06	0.66*	0.30*	0.58*	1.00	0.89*	0.42*
ECah	-0.38*	0.07	0.62*	0.30*	0.59*	0.89*	1.00	0.39*
Dispersion	-0.01	-0.08	0.25*	0.62*	0.69*	0.42*	0.39*	1.00

† TWI, Topographic wetness index.

‡ ECav, ECa in vertical direction.

§ ECah, ECa in horizontal direction.

¶ \*, Significant at 95% of confidence interval.

**APPENDIX D. THE GYPSUM APPLICATION RATE FOR THE FIELD STUDY AND COSTS: EXAMPLE CALCULATION IN PAPER 4**

1 acre furrow slice is the volume of soil in an acre of topsoil at 6 2/3 inches deep.

The estimated weight of soil in 1 acre furrow slice is  $2 \times 10^6$  lbs

Table D1. Obtain the bulk density of soil using data from Soil Salinity Laboratory Staff (1954).

	Area (ft <sup>2</sup> )	Depth (ft)	Volume (ft <sup>3</sup> )	Furrow slice (lbs)	Bulk density (lbs/ft <sup>3</sup> )	Pb (g/cm <sup>3</sup> )
1 acre	43560	0.5	21780.0	2000000	91.827	1.4731
1/2 acre	21780	0.5	10890.0	1000000	91.827	
1/4 acre	10890	0.5	5445.0	500000	91.827	
1/20 acre	2178	0.5	1089.0	100000	91.827	

Table D2. Predict soil sample area and mass in the study plot (40 ft \*40 ft at a depth of 1 ft).

Distance (m)	Area (m <sup>2</sup> )	Area (ft <sup>2</sup> )	Depth (ft)	1 UNIT volume (ft <sup>3</sup> )	Bulk density (lbs/ft <sup>3</sup> )	The mass of soil (lbs)
12.2	148.84	1601.52	1	1601.5184	91.827	147063

If 1 meq/100g of exchangeable Na on soil exchange site is required to be replaced by Ca

Set the volume here as 1 UNIT = 1601 ft<sup>3</sup>.

Table D3. Gypsum required application rate in our field.

The mass of soil (lbs)	The mass of soil (kg/UNIT)	Total charge (cmol/UNIT)	The Ca required to replace total charge (Kg Ca/UNIT)	The gypsum that can provide Ca (kg/UNIT)	Convert gypsum unit (Mg/UNIT)	Convert gypsum unit (Mg/m <sup>3</sup> )	Convert gypsum unit (lbs/acre inch)
147063	66766.4	66766.4	13.353	57.310	0.057	0.0013	<b>286.504</b>

**Calculation steps:**

Ca percentage in gypsum =  $40/172 = 23.3\%$

$$1 \text{ meq } (100\text{g})^{-1} = 1 \text{ cmol}_{(+)} \text{ kg}^{-1}$$

Assumption: If 1 meq (100g)<sup>-1</sup> of exchangeable Na on soil exchange site is required to be replaced by Ca from gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O).

Step 1: Study volume of soil: 12.2 m \*12.2 m \* 0.3 m = 44.652 m<sup>3</sup> =1602 ft<sup>3</sup>



The bulk density is estimated as 91.827 lbs ft<sup>-3</sup> (1.47g cm<sup>-3</sup>) from the Table in estimation of gypsum application from U.S. Salinity Laboratory Staff (1954).

The mass of soils in the study area: 91.827 lbs ft<sup>-3</sup> \* 1602 ft<sup>3</sup> = 147063 lbs = 66766 kg

Step 2: Total charge: the meq 100g<sup>-1</sup> (cmol<sub>(+)</sub> kg<sup>-1</sup>) in study area of soil is needed to be replaced.

$$\left(\frac{66766 \text{ kg}}{\text{sample area}}\right) * \left(\frac{1 \text{ cmol}_{(+)}}{\text{kg}}\right) = 66766 \text{ cmol}_{(+)} (\text{sample area})^{-1}$$

Step 3: The amount of Ca required to replace the total charge in Step 2.

$$\left(\frac{66766 * \text{cmol}_{(+)}}{\text{sample area}}\right) * \left(\frac{1 \text{ Eq}}{100 \text{ cmol}_{(+)}}\right) * \left(\frac{1 \text{ mol}}{2 \text{ Eq}}\right) * \left(\frac{40 \text{ g}}{\text{mol}}\right) * \left(\frac{1 \text{ kg}}{1000 \text{ g}}\right) = 13.353 \text{ kg Ca (sample area)}^{-1}$$

Step 4: The amount of gypsum that can provide the Ca required in Step 3.

$$\left(\frac{13.353 \text{ kg Ca}}{\text{sample area}}\right) * \left(\frac{\text{kg gypsum}}{0.233 \text{ kg Ca}}\right) = 57.310 \text{ kg gypsum (sample area)}^{-1}$$

Step 5: Convert the unit of gypsum in Step 4.

$$\left(\frac{57.310 \text{ kg gypsum}}{\text{sample area}}\right) / 1000 = 0.057 \text{ Mg (sample area)}^{-1}$$

Step 6:  $\frac{0.057 \text{ Mg (sample area)}^{-1}}{(1602 \text{ ft}^3) * 0.0283} = 0.0013 \text{ Mg m}^{-3}$

$$\frac{0.0013 \text{ Mg} * 2204.6}{0.00973} = 286.504 \text{ lbs (acre inch)}$$

Step 7: Example in the following Table: Assume all Na in Na% = Na<sub>ex</sub>, the goal is to reduce

Na% to 5%. Then the amount of the Na needed to be replaced is the difference to 2.181 meq 100g<sup>-1</sup> (the amount of Na at 5%).

For example: site A2, the Na is 3.116 meq 100g<sup>-1</sup>, the Na% = 6.831% > 5%. The gypsum application rate is based on the value obtained in Step 6.

The amount of Na to bring Na% from 6.831 to 5% is 3.116 - 2.181 = 0.935 meq 100g<sup>-1</sup>

According to Step 6, to replace 1 meq  $100\text{g}^{-1}$  of Na, gypsum required is 286.504 lbs (acre inch). Then at A2, the gypsum required is  $286.504 \text{ lbs (acre inch)} * 0.935 \text{ meq } 100\text{g}^{-1} = 268 \text{ lbs (acre inch)}$

Convert unit:  $268 \text{ lbs (acre inch)} / (2000 \text{ lbs/ton}) = 0.134 \text{ tons (sample area)}^{-1}$

Convert the gypsum unit to tons gypsum  $\text{acre}^{-1}$

$0.134 \text{ tons} / [(40\text{ft}*40\text{ft})/(43560 \text{ ft}^2/\text{acre})] = 3.648 \text{ tons gypsum acre}^{-1}$

U.S. Salinity Laboratory Staff recommended to apply gypsum by a factor of 1.25 times and gypsum price is about 240 \$ gypsum  $\text{tons}^{-1}$

The cost of gypsum in A2:  $3.648 \text{ tons gypsum acre}^{-1} * 1.25 * 240 \text{ \$ gypsum tons}^{-1} = 1094 \text{ \$ acre}^{-1}$

The detailed information for the calculation can be found in the following Appendix

Figure. Detailed gypsum application rate for study area and the calculation for plot A2 is as footnotes in the Figure.

A	B	C	D	E	F	G	H	I	J	K	L	M
	Point	Depth	Measured Na (meq/100g)	Measured Na%	Total Na to replace and to reduce Na to 5%	Gypsum unit (Mg/UNT)	Gypsum unit (Mg/m <sup>3</sup> )	Gypsum unit (lbs/sample area-inch)	tons of gyp per sample area	tons gyp/acre	x 1.25	\$240 gyp/ton
1			<b>2.181</b>			<b>0.057</b>	<b>0.001</b>	<b>286.504</b>				
2	A2	1 ft	3.116	6.831	0.935	0.0536	0.0012	268	0.134	3.648	4.560	
3	A3	1 ft	2.329	5.420	0.148	0.0085	0.0002	43	0.021	0.579	0.723	
4	A4	1 ft	3.477	7.761	1.296	0.0743	0.0016	371	0.186	5.054	6.318	
5	C2	1 ft	2.412	5.421	0.231	0.0132	0.0003	66	0.033	0.900	1.125	
6	D2	1 ft	<b>2.181</b>	<b>5.047</b>	0.000	0.0000	0.0000	0	0.000	0.000	0.000	
7	D3	1 ft	2.049	4.929	0.000	0.0000	0.0000	0	0.000	0.000	0.000	
8	D4	1 ft	3.170	8.070	0.989	0.0567	0.0013	283	0.142	3.858	4.823	
9	D10	1 ft	5.864	14.073	3.683	0.2111	0.0047	1055	0.528	14.362	17.953	
10	D11	1 ft	3.984	9.563	1.803	0.1033	0.0023	517	0.258	7.031	8.789	
11	I2	1 ft	3.717	7.863	1.536	0.0880	0.0019	440	0.220	5.990	7.487	
12	N2	1 ft	3.424	5.922	1.243	0.0712	0.0016	356	0.178	4.846	6.058	
13	N6	1 ft	4.544	7.290	2.363	0.1354	0.0030	677	0.338	9.215	11.519	
14	N7	1 ft	3.720	5.933	1.539	0.0882	0.0019	441	0.220	6.003	7.503	
15	N29	1 ft	3.184	6.764	1.003	0.0575	0.0013	287	0.144	3.912	4.891	
16	O3	1 ft	3.869	5.924	1.688	0.0967	0.0021	484	0.242	6.582	8.227	
17	O8	1 ft	6.962	10.262	4.781	0.2740	0.0060	1370	0.685	18.645	23.306	
18	O26	1 ft	3.093	7.353	0.912	0.0523	0.0012	261	0.131	3.557	4.447	
19	O27	1 ft	4.829	13.968	2.648	0.1518	0.0033	759	0.379	10.329	12.911	
20	O29	1 ft	4.259	11.794	2.078	0.1191	0.0026	595	0.298	8.105	10.131	
21	O30	1 ft	2.209	8.561	0.028	0.0016	0.0000	8	0.004	0.111	0.138	
22	O31	1 ft	5.764	9.636	3.583	0.2054	0.0045	1027	0.513	13.975	17.469	
23	P20	1 ft	3.538	6.136	1.357	0.0778	0.0017	389	0.194	5.292	6.615	
24	Q1	1 ft	4.624	6.763	2.443	0.1400	0.0031	700	0.350	9.528	11.910	
25	Q29	1 ft	3.629	8.789	1.448	0.0830	0.0018	415	0.207	6.757	8.446	44484.0 6

D1: the basic Na (meq/100g) at 5% of Na  
H1: the gypsum rate from Step 6  
D2: Measured soil actual Na (meq/100g)  
F2 = D2 - D1  
J2 = J2/2000 (convert from lbs to tons. 2000lbs/ton)  
K2 = J2/(40\*40/43560) (40 ft is the sample grid size, 43560 ft<sup>2</sup>/acre, so the sample area = 40\*40/43560)  
L2 = K2 \* 1.25  
G1: the gypsum rate from Step 5  
I1: the gypsum rate from Step 6  
E2: Measured soil Na% that are > 5%  
H2 = F2 \* H1  
I2 = F2 \* I1  
M2 = 240 \* L2  
M25 = SUM (L2:L25)\*240

Fig. D1. Calculation of the gypsum application rate and cost for the plots with Na% above 5%.