Effect of Soil ESP and Salinity on Soil Atterberg Limits, Swelling and Hydrologic Properties

By

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DEDICATION

I would like to dedicate this to my friends and family.

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I would like to acknowledge the members of my PhD Committee, Will Bleam my major advisor, Francisco Arriaga my co-advisor and Doug Soldat, Alfred Hartemink and Will Likos for serving on my committee. I would like to acknowledge the water science and engineering lab for allowing me to run 100s of samples through their ICP. I would like to acknowledge Jim Millnar of Precision Soil Management for help collecting soils in South Dakota. I would like to thank Wendell Hutchins from North Carolina State University for the Cecil soil. I would like to thank Joel Bell for sending Fargo soil from North Dakota State University. I would like to thank Aaron Daigh in allowing the use of water retention and hydraulic conductivity data from Klopp 2015

ABSTRACT

Soil sodicity is a global issue decreasing economic outputs of soils. High solution sodium adsorption ratio (SAR) and low EC increases swelling of smectite clay and causes breakdown of soil aggregates. The effect of solution composition on soils has been commonly measured by saturated hydraulic conductivity which decreases as solution EC decreases and SAR increases with the effects most pronounced on smectite clay dominant soils, which also is the only clay type that has interlayer swelling from exchangeable sodium. Currently soil physical properties are not used to classify soils that are sensitive to soil sodicity. The objectives of this dissertation, are 1) to determine how properties related to soil swelling and hydrology change on soils of a range of clay mineralogy, 2) determine a soil physical property that can discriminate between soils that are sensitive to high ESP levels from soils that are not sensitive to soil sodicity and 3) to predict the change of soil properties in response to solution EC and SAR. Soil Atterberg limits, shrinkage and water retention were measured under soil ESP and EC combinations on soils of a range of textures and clay mineralogy, using a dry sodium carbonate treatment and mixtures of sodium and calcium chloride solutions. Soil saturated hydraulic conductivity decreased, and shrinkage, water retention and Atterberg limits increased in smectitic soils. Smectitic soils had a larger change in soil hydraulic conductivity and are the only soils that had pronounced changes in soil physical properties related to swelling from high ESP and low EC. Measuring soil liquid limit or water retention at points of -1/10 or -1/3 bar in a low EC-low ESP and a low EC-high ESP state can distinguish soils sensitive to sodicity from soils not sensitive to sodicity. Existing models to predict soil hydrologic properties performed poorly on smectitic soils. Accounting for the smectite content by cation exchange capacity improved prediction of soil hydrologic properties on smectitic soils. Soils that are smectitic can be rapidly identified by

measuring soil swelling related property and have a narrower range of irrigation water qualities acceptable for use before soil hydrologic properties change.

CHAPTER 1

Effect of Soil Exchangeable Sodium Percentage and Salinity on Soil Atterberg Limits and Coeficient of Linear Expansion (COLE) Implications for Soil Sodium Sensitivity

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Submitted to Geoderma

Abstract

Soil sodicity is defined by the Food and Agricultural Organization (FAO) as a soil having an exchangeable sodium percentage (ESP) greater than 15, a saturated paste extract electrical conductivity (EC) less than 4 dS m^{-1} and a high pH (8.2 or greater). Soils containing smectite clays have been found to be most sensitive to soil sodicity although little research exists directly relating soil sodicity to clay swelling under varying levels of salinity and ESP. The goal of this study is to determine a soil swelling related measurement that can be a proxy to determine soil sensitivity to exchangeable sodium. This study examined the response of three smectitic soils treated with salt solutions having concentrations ranging between 5 and 40 $mmol_c$ dm^{-3} and ESP levels between 0 and 50 % to create differing degrees of sodicity. Whole soil Atterberg limits and shrinkage potential were measured prior to and after treatments. Liquid limit, plasticity index and shrinkage potential increased for all three soils after treatment with a salt concentration of 5 $mmol_c$ dm^{-3} at an ESP of 25 and 50% and 10 $mmol_c$ dm^{-3} at an ESP of 50 %. Comparing liquid limit of low salinity treatment at 50 % ESP to low salinity 0% ESP reveal the presence of swelling smectite clay and the sensitivity of the soils to sodicity.

Introduction

Soil sodification and salinization are global issues occurring in both irrigated and non-irrigated agriculture. Soil sodicity complicates the management of soil salinity and water by decreasing the rate of water movement through soil (Quirk and Schofield, 1955). Many studies evaluate changes in saturated hydraulic conductivity, dispersion and aggregate stability under varying salinity and exchangeable sodium levels of applied water (e.g., Rengasamy et al., 1984 and McNeal et al., 1966a). These studies found that some soils are insensitive to the sodicity of irrigation water, whereas others are very sensitive to conditions of low soil solution electrical conductivity (EC) and high exchangeable sodium percentage (ESP).

Soils that contain high amounts of smectite clay appear to be most sensitive to exchangeable sodium, exhibiting changes in saturated hydraulic conductivity, aggregate stability, and clay dispersion (Crescimanno et al., 1992; McNeal et al, 1966. and USSL Staff, 1954). Identifying soil properties responsive to the swelling clay content of a soil and any changes to these properties with increasing ESP could help quantify sodium sensitivity. Atterberg limits, and coefficient of linear extensibility (COLE) are both physical properties responsive to the swelling clay fraction of the soil. Their use indicators of soil sodium sensitivity are the topic of this study.

Smectite clays are the only clay mineral group that show an increase in Atterberg limits and free swelling in response to an increase in ESP (Prakash and Sridharan, 2004; and Bain, 1971). Plasticity charts that plot soil plasticity index PI[1] as a function of liquid limit (LL) can reveal the effect of clay mineralogy on soil plasticity because smectite clays have much higher LL and PI values than other clay minerals. (Bain, 1971). There is a large difference in the swelling behavior and plasticity of calcium-smectite compared to sodium saturated smectite (Bain, 1971). These differences, however, depend on salinity; sodium smectite behaves like calcium smectite at high salinity because the high osmotic potential of saline solutions prevents water from entering smectite clay interlayers (Katsumi et al., 2008).

Increases in soil shrink-swell capacity have been observed for smectitic soils after treatment with solutions of high SAR[2] (expression (1)) and low EC as revealed using COLE clod and rod methods (Chaudhari, 2001; Crescimano et al., 1992 ; Malik et al., 1992).

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[1] The plasticity index PI is defined as the difference between liquid limit LL and plastic limit PL: PI = LL – PL.

[2] The SAR is calculated using millimolar concentrations of $Na^{+}Ca^{2+}$ and Mg^{2+}

$$SAR = \frac{Na^{+}}{\sqrt{Mg^{2+}+Ca^{2+}}} \tag{1}$$

Chaudhari et al., (2001) and Malik et al., (1992) found an increase in soil COLE as ESP increased and salt concentration decreased for soils ranging from a silt loam with 23% clay to a clay texture with 69 % clay for all soils that contained some smectite clay. The soil COLE was found to have a large increase in a vertisol at an ESP level as low as 10 % in a soil with 55% clay (Crescimano et al., 1992).

Our first objective is to quantify changes in soil swelling properties across a gradient of salt concentrations and ESP values. Our second objective is to evaluate whether one or more of these physical properties can distinguish soils based on their sensitivity to exchangeable sodium.

Materials and Methods

Soil Collection

Three soils with smectitic mineralogy were collected near Redfield, South Dakota. A sample of argillic horizon representative of the Harmony series (Fine, smectitic, frigid Pachic Argiudolls) was collected at 44.9827 N, 98.5088 W from 30-50 cm depth. A sample of Natric horizon representative of the Aberdeen soil series (Fine, smectitic, frigid Glossic Natrudolls) was collected at 44.9553 N, 98.4426 W from 25-45 cm depth. A sample representative of the Exline soil series (Fine, smectitic frigid Leptic Natrudolls) was collected from 44.9550 N, 98.4229 W from 15 to 40 cm depth. These soils were selected because they were formed from the same parent material but have different chemical properties and horizons due to landscape position and water flow patterns. X-ray diffraction was measured on clay fraction by dispersing soil with 50 g/l sodium hexametaphosphate and removing the top 10 cm of liquid after all particles coarser than 2 um were settled out of top 10 cm. After samples were dried and crushed, X-ray diffraction was then measured on the homogenized < 2um fraction.

Soil Characterization

Particle size analysis was measured using the pipette method (Deshpande and Telang, 1950). Exchangeable cations were measured using a 1 molar CsCl extract. Cations present in saturated paste extract, 1:1 extract and CsCl extract were measured using ICP-OES Perkin Elmer Optima 4300 DV. Electrical conductivity and sodium adsorption ratio were measured using a saturated paste and 1:1 extract. Atterberg limits were determined on the soils as they were collected and conditioned with deionized (DI) water (Casagrande, 1932). Soil COLE was measured by using the rod method for soils conditioned with DI water (Schafer and Singer, 1976).

Cation Exchange Data Verification

Soil columns of Aberdeen, Exline and Harmony soils were treated with solutions of $NaCl-CaCl_2$ with SAR values of 5 and 17 and salt concentrations of 5, 10, 20 and 40 $mmol_c\ dm^{-3}$. Once the outflow EC was equal to the inflow EC, the soil sample was air dried and passed through a 2-mm sieve to measure extractable cations. A sample of the outflow solution was kept to determine cations present in solution phase and ESP was measured using a CsCl extract. The entire exchange data was fit for each soil with the Vanselow equation (Appendix 1 and Appendix 2) (Vanselow 1932). The confidence intervals were determined using bootstrap method creating replicates of 10 (Efron, 1987). Estimated (Na^+, Ca^{2+}) exchange selectivity coefficients ranged from 0.19 to 0.44 for these three soils (Appendix 1 and Appendix 2). These values are within the range of values listed for soils and clay minerals (Amrhein and Suarez, 1991) and are slightly lower than values listed on Yolo loam and three soils from India ranging between 0.3 and 0.8 (Gupta et al., 1984 and Jensen and Babcock, 1973).

Column Treatments

A (Na^+, Ca^{2+}) exchange selectivity coefficient of 0.22 was used to make solution treatments to create ESP levels of 0, 6, 15, 25 and 50 at salt concentrations of 5, 10, 20 and 40 $mmol_c\ dm^{-3}$ $meq\ L^{-1}$ to create a gradient of ESP and salt concentration. The soils were treated until outflow EC was equal to inflow EC. The treating with $NaCl$-$CaCl_2$ solutions based upon selectivity constant created ESP values within 60% of desired treatment level except for 5 $mmol_c\ dm^{-3}$ treatments which created SAR values less than half of desired solution SAR levels after 2 months of treatment with ESP 25 solution at 5 $mmol_c\ dm^{-3}$. Low salinity and high ESP treatments required a long time (months) to reach desired EC; therefore we developed a more rapid dry treatment to produce high ESP and low salinity levels.

Dry Treatment Procedure

Given the low hydraulic conductivity and long time needed to treat the soil, the treatments at 5 $mmol_c\ dm^{-3}$ at all ESP levels and 10 $mmol_c\ dm^{-3}$ at an ESP 50 were made by applying Na_2CO_3 to a dry calcium saturated soil that had been leached with $CaCl_2$ at the desired salinity level (Bain 1971). Soils were calcium saturated by leaching in columns with 5 pore volumes of 0.5 M $CaCl_2$ and then were leached with 5 or 10 $mmol_c\ dm^{-3}$ $CaCl_2$ solution until the desired outflow salinity level occurred.

The amount of Na_2CO_3 added was calculated by multiplying the desired ESP times soil CEC plus an additional amount to account for the amount of sodium present in solution. The amount of sodium present in solution was determined assuming a 0.55 saturated water content and cation exchange equilibrium in solution at the desired ESP. The amount of Na_2CO_3 added is listed in (Appendix 3). After the Na_2CO_3 was added, the soils were brought to saturation by adding distilled, DI water and were allowed to equilibrate at water content close to saturation for 24 hours. Adding the Na_2CO_3 provided sufficient carbonate to precipitate the desired level of calcium which was observed in the results (Table 4). The Na_2CO_3 increased ESP to the desired level, although salinity level was a little higher than level that was desired (Table 5). For example to create an ESP treatment of 50% on the Harmony soil 10.826 g of Na_2CO_3 was added to the soil. The measured ESP levels were consistently higher than estimated ESP levels based on sodium mass balance accounting for both the exchange complex and solution (Table 4).

Atterberg Limits and Soil COLE

Atterberg limits were measured by wetting the soil with the salt solution with which they were originally equilibrated with the exception of Na_2CO_3 treatments which were wetted with DI water. The salinity levels employed were 5 $mmol_c$ dm^{-3} meq cation l^{-1} (0.63 dS m^{-1} to 0.68 dS m^{-11}), 10 meq cation (1.26-1.35 dS m^{-1}), 20 $mmol_c$ dm^{-3} meq cation l^{-1} (2.52-2.7 dS m^{-1}) and 40 $mmol_c$ dm^{-3} (5.0.-5.4 dS m^{-1}) (Harned and Owen, 1964). Plastic limits were determined as the minimum water content required to form a plastic material by rolling the soil on a glass sheet until the soil began to crack when forming a 4.76 mm rod. Liquid limits were measured using a percussive liquid limit device by mixing soil with water and recording number of drops, and water content at three drop counts between 15 and 45 drops times using standard procedures (Casagrande, 1932). Liquid limit was calculated as logarithmic regression fitting for gravimetric water content at 25 drops. Plasticity index was calculated as the difference between measured liquid and plastic limits. Three replicates of each test were run.

Soil COLE was measured using rod method by wetting with the salt solution the soil was initially equilibrated to. (Schafer and Singer, 1976). Ten replicates of each treatment were used to measure soil COLE.

Statistical analysis

Statistical Analysis System SAS 9.4 was for analysis of variance ANOVA using a randomized block design. An ANOVA was run on all three soils combined together and then on individual soils for salt concentration, ESP and Salt Concentration*ESP effects. A statistically significant difference occurred at $P < 0.05$. A confidence interval of the ESP 0 and ESP 50 treatment was used to determine the differences between the high soil ESP treatment and the low ESP treatment at each salinity level for a given soil. Statistical significance occurred at alpha value of 0.05.

Results

All three soils used in this study are classified as belonging to the smectitic mineralogy class. The Aberdeen, Exline and Harmony soils were primarily smectite and illite with small amounts of quartz and kaolinite in the soil clay fraction.

This study directly measures water uptake by swelling clay minerals using whole-soil Atterberg limits and COLE. Earlier, McNeal and others (McNeal et al., 1966; McNeal, 1968b) indirectly estimated swelling-clay water uptake by: 1) quantifying smectite clay using XRD supplemented by other measurements (McNeal, 1968a), 2) assuming ESP correlates with the fraction of Na-saturated interlayers, and, finally, 3) assuming soil smectite swelling behaved the same as the Na-saturated smectite specimen used by Norrish (1954). Despite the uncertainty of quantitative XRD (McNeal, 1968a) and the domain-model assumption that smectite segregates into Na-saturated and Ca-saturated interlayers, these two assumptions are reasonable approximations. The final assumption, that soil smectite interlayer behave like the Wyoming bentonite described by Norrish (1954), is questionable as results presented below will demonstrate.

The Exline soil as sampled had the greatest ESP and significantly higher liquid limit, plasticity index, and COLE value than the other two soils from the same parent material (Table 2, Table 3 and Figure 1). Figure 1 shows that natural sodium smectite has a much higher plasticity than natural calcium smectite and, furthermore, when pure smectite clays are compared to the untreated Harmony, Aberdeen and Exline soils, the LL and PI of the pure clays are much higher than the smectitic soils used in this study.

The treatments used in this study were designed to create different levels of ESP in the three soils (Aberdeen, Exline and Harmony). After treatment soil LL values were similar for a given ESP and salt concentration treatment (Appendix 4). Whole-soil liquid limits gradually increased as soil ESP increased for low salinity treatments whereas it did not change significantly for high salinity treatments (Figure 2). High salinity draws water from swelling clay interlayers, preventing free swelling. The whole-soil LL was significantly different for all three soils for ESP effect and EC*ESP effect with low EC and high ESP levels increasing the soil LL based upon the ANOVA.

Increasing ESP to 25% or above increased LL in all three soils at the lowest salt concentration of 5 $\text{mmol}_c\ \text{dm}^{-3}$, and when the ESP was 50 % the LL increases even at a second lowest salt concentration of 10 $\text{mmol}_c\ \text{dm}^{-3}$ (Figure 2 and Appendix 4). The increase in LL from the low EC high ESP treatments is from active smectite in the soil as can be identified by X-ray diffraction.

The (LL, PI) relations for all three treated soils plotted above the A-line which the geotechnical community uses to distinguish between silt and clays based on plasticity. The LL and PI of the 5 mmol$_c$ dm^{-3} ESP 50 treatment was drastically greater than 5 mmol$_c$ dm^{-3} ESP 0 treatment for all three soils (Figure 3, Figure 4 and Figure 5). Increasing soil ESP while maintaining low EC increases the distance above the A line although all the points are above the A line which means the soil is classified as a clay.

Soil COLE values increased with LL and PI values with a linear relationship between COLE and plasticity index and liquid limit (R^2 of 0.55). All three soils had an increase in whole soil shrinkage at salt concentrations of 5 and 10 mmol$_c$ dm^{-3} at an ESP value of 50 % and at 5 mmol$_c$ dm^{-3} at an ESP of 25% (Appendix 4). Soil shrinkage also increases with low salt concentration and ESP of 25% and 50% in these soils that are characterized as being smectitic.

Discussion

The behavior of the clay fraction changed in response to ESP in the soil specimens used in this study. Increasing ESP while maintaining low EC caused increases in the swelling and plasticity of all the three smectitic soils. Whole-soil LL values increased as ESP increased, and salt concentration decreased, as was also found for pure smectite (Katsumi et al., 2008). The increase in LL with ESP is similar to the differences between Na-saturated smectite and Ca-saturated smectites, although to a much lesser degree (Figure 2). Soil shrinkage also differed for the untreated soils with a COLE value of 0.135 (0.44 COLE to clay ratio) in Harmony soil, increasing to 0.203 (0.44 COLE to clay ratio) in Exline soil (Table 3).

Dividing the PI by clay content yields clay activity A, Harmony as sampled had an activity A= 0.61; Aberdeen as sampled had an activity of A= 0.56; and Exline as sampled had an activity of A= 0.81. As ESP increased from 0 to 50% treatment at 5 mmol$_c$ dm^{-3} soil clay activity increased from 0.74 to 1.03 for Harmony soil, from 0.50 to 0.87 for Aberdeen soil, and from 0.56 to 0.93 for Exline soil (Appendix Table 3). The activities of these soils for the ESP 0 treatment were considered to be inactive clays, with the ESP 50 treatment increasing their activity to be normal clays at 5 $\text{mmol}_c\ \text{dm}^{-3}$ (Skempton, 1953). Assuming that these soil series are smectite dominant and the behavior of the smectite in the soil is as McNeal assumed from Norrish 1954 the soils would be expected to have a much larger than was observed increase in clay activity.

The activity of calcium montmorillonite is typically 1.5 and sodium montmorillonite is typically 7.2 which is much greater than for the soils used in this study that are considered to be smectitic (Skempton, 1953). Assuming ESP is the percent of the layers that are sodium saturated and behave as sodium montmorillonite and the remaining layers are calcium saturated and behaved as calcium montmorillonite, the increase in clay activity would be much greater than was found in the soils used in this study. We conclude the swelling clay in these soils is much less active than pure smectite specimens and the assumption made by McNeal et al., 1966 that soil clays behave like Wyoming bentonite is unfounded. The important part in determining clay sensitivity to exchangeable sodium is to observe an increase in the soil LL between the low salinity, low ESP treatment and the low salinity, high ESP treatment.

Soil shrink-swell potential also increased at high ESP and low salinity treatments because of the swelling of smectite clays present in the soil. Soil shrink-swell potential did not increase until ESP levels greater than 15 % and low salt concentrations (i.e., <10 $\text{mmol}_c\ \text{dm}^{-3}$ meq L^{-1}). Soil shrinkage potential increased at high ESP levels and low EC levels as also was found in previous studies that measured soil shrinkage potential on soils (Klopp, 2015; Crescimanno et al., 1992; Malik et al., 1992). Klopp et al. (2018) also observed a relatively small increase in soil COLE values between solution SAR values that were applied to a smectitic soil with a similar clay content to these soils (0.15 vs 0.17) soil COLE value between SAR treatment of 0 and 20 and a solution EC of 0.5 dS m^{-1}.

Soil COLE/clay percentage ratio increased from 0.54 to 1.02 for Harmony soil from 0.50 to 0.70 for Aberdeen soil and from 0.49 to 0.88 for Exline soils between ESP level of 0 and 50 for 5 $mmol_c$ dm^{-3} treatment. Soil COLE changed in a similar manner as the soil plasticity index; as ESP increased at low EC levels. Shrinkage/swelling and degree of plasticity had a consistent relationship across salinity and ESP treatments that were studied in these soils. Our data agrees with what was reported by others on extracted soil clay fraction and pure clay specimens with a gradual increase in swelling as ESP increases and EC decreases. (McNeal et al., 1966 ; El-Swaify and Henderson, 1967) The increases in shrinkage with an increase in ESP at low salinity levels indicate the presence of smectite in these soils which is the soil clay mineral susceptible to sodicity.

Soil liquid limit had the largest differences between the salt concentration vs salinity treatments that were applied to the soils. Properties measured to indicate whole soil swelling under highly sodic soil conditions compared to low salinity conditions increased to a very large degree (Table 5). There is no threshold at which an abrupt change occurs, instead the changes are gradual (McNeal, 1968; El Swaify and Henderson, 1967; McNeal et al., 1966 a and Quirk and Schofield, 1955). Soil liquid limit had the largest response and would be the best indicator of a soil that is sensitive to exchangeable sodium of the soil properties that we evaluated. Comparing the liquid limit of a soil that is brought to a high ESP to a control (calcium saturated) at low salinity (e.g., 5 $mmol_c$ dm^{-3}) resulted in a large statistical difference in these soils, a direct result of smectite clay swelling.

The difference in liquid limit between the ESP 50 treatment and ESP 0 treatment gradually become larger as soil salinity is reduced showing a direct connection to the osmotic effect of solution on smectite (Katsumi et al., 2008).

Conclusions

Properties measured to indicate soil swelling increase under sodic soil conditions (i.e., low EC, high ESP) and show a similar increase but to a lesser degree compared to pure bentonites. An increase in the liquid limit from the calcium state to the sodic state identifies clay that is behaving as a smectite within the soil taking water into the interlayer. Increasing the active smectite clay content increases the likelihood hydraulic conductivity will decrease due to sodicity leading to smectite clay content increasing change in this property (Klopp, 2015; McNeal et al., 1966). The clay activity of pure smectites was much greater than the smectitic soils that were used in this study. A change in properties related to soil swelling from high ESP shows smectite is presence in these soils providing evidence they are sensitive to sodicity.

Soils that contain smectitic clays are productive agricultural soils found throughout the world that have dynamic soil physical properties. Increased swelling of smectite from ESP creates issues when managing soil water and the solutes dissolved in it. Measuring soil liquid limit on soils in a calcium low EC state and a high ESP low EC state can rapidly identify soils that contain smectite behavior in their soil clay fraction. Smectitic soils require the most careful management when selecting irrigation waters to use.

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Tables and Figures

Table 1. Basic chemical properties of untreated soils.

Soil	EC (saturated paste) dS m^{-1}	SAR (saturated paste)	EC 1:1 Extract dS m^{-1}	SAR 1:1 Extract	CEC cmol kg^{-1}	ESP %
Aberdeen	0.660	8.94	0.650	6.73	21.1	11.4
Exline	3.15	18.0	1.99	0.450	18.7	37.0
Harmony	0.590	1.35	0.390	0.970	25.4	0.967

Table 2. Particle size distribution and organic matter percentage (OM) of the Exline, Aberdeen and Harmony soils.

Soil	Sand (%)	Silt (%)	Clay (%)	OM (%)
Aberdeen	1.90	61.2	36.9	3.40
Exline	3.10	61.4	35.5	2.90
Harmony	10.1	59.0	30.9	4.50

Table 3. Liquid limit, plastic limit, plasticity index, clay activity, COLE and COLE/clay content for Aberdeen, Exline and Harmony soils as they were collected.

Soil	Liquid Limit (%)	Plastic Limit (%)	Plasticity Index (%)	Clay activity	COLE	Cole/Clay content
Aberdeen	51.9	27.5	24.3	0.570	0.179	0.485
Exline	59.2	30.7	28.5	0.820	0.203	0.571
Harmony	48.2	29.1	19.1	0.614	0.135	0.442

Table 4. Soil Treatments, electrical conductivity (EC) of (1:1 soil to water extract) and exchangeable sodium percentage (ESP) for Aberdeen, Exline and Harmony soils.

Soil	Aberdeen		Exline		Harmony	
Treatment	EC 1:1 (dS m^{-1})	ESP (%)	EC1:1 (dS m^{-1})	ESP (%)	EC1:1 (dS m^{-1})	ESP (%)
5 mmolc dm^{-3} ESP 0	0.440	1.00	0.680	2.50	0.580	0.000
5mmolc dm^{-3} ESP 6	1.94	5.10	0.880	8.00	1.56	7.70
5 mmolc dm^{-3} ESP 15	1.04	12.1	1.39	17.5	1.11	19.0
5 mmolc dm^{-3} ESP 25	1.70	20.1	1.38	36.5	2.63	38.8
5 mmolc dm^{-3} ESP 50	1.69	63.2	1.77	47.6	1.95	79.1
10 mmolc dm^{-3} ESP 0	0.821	0.00300	0.770	3.60	0.480	0.600
10 mmolc dm^{-3} ESP 6	1.29	6.28	1.10	10.5	1.05	4.60
10 mmolc dm^{-3} ESP 15	0.820	13.3	1.06	16.4	0.900	9.10
10 mmolc dm^{-3} ESP 25	1.13	21.1	1.05	14.1	1.14	17.1
10 mmolc dm^{-3} ESP 50	2.53	88.2	1.60	49.6	4.39	72.0
20 mmolc dm^{-3} ESP 0	1.14	0.000	1.53	0.900	1.23	1.70
20 mmolc dm^{-3} ESP 6	1.34	3.25	0.960	8.70	1.23	3.10
20 mmolc dm^{-3} ESP 15	1.23	14.1	1.22	11.7	1.47	11.5
20 mmolc dm^{-3} ESP 25	1.44	26.8	1.81	20.3	1.30	19.0
20 mmolc dm^{-3} ESP 50	1.46	35.2	2.08	36.6	1.73	27.0
40 mmolc dm^{-3} ESP 0	2.10	1.15	2.09	2.10	2.28	0.900
40 mmolc dm^{-3} ESP 6	2.07	6.38	2.00	6.70	2.25	4.40
40 mmolc dm-3 ESP 15	1.59	13.7	1.77	17.5	2.36	15.7
40 mmolc dm^{-3} ESP 25	2.16	21.9	2.99	18.6	1.92	19.9
40 mmolc dm^{-3} ESP 50	1.44	30.5	3.40	50.2	2.01	33.0

Table 5. Liquid limit (LL), and confidence interval for Aberdeen, Exline and Harmony soils at 5 mmolc dm^{-3} ESP 0 treatment (Calcic), 5 mmolc dm^{-3} ESP 50 treatment (Sodic), 10 mmolc dm^{-3} ESP 0 treatment, 10 mmolc dm^{-3} ESP 50 treatment, 20 mmolc dm^{-3} ESP 0 treatment, 20 mmolc dm^{-3} ESP 50 treatment, 40 mmolc dm^{-3} ESP 0 treatment and 40 mmolc dm^{-3} ESP 50 treatment Alpha equal 0.05.

Treatment	Aberdeen		Exline		Harmony	
	LL (%)	CI	LL (%)	CI	LL (%)	CI
5 mmolc dm^{-3} ESP 0	41	0.87	46	1.60	47	0.94
5 mmolc dm^{-3} ESP 50	58	1.1	56	1.7	57	2.0
10 mmolc dm^{-3} ESP 0	44	0.092	43	1.1	45	0.18
10 mmolc dm^{-3} ESP 50	61	0.020	52	0.78	53	1.1
20 mmolc dm^{-3} ESP 0	44	0.53	44	1.1	44	1.1
20 mmolc dm^{-3} ESP 50	48	.23	48	1.3	47	0.092
40 mmolc dm^{-3} ESP 0	48	0.11	45	0.80	46	1.3
40 mmolc dm^{-3} ESP 50	48	0.78	48	1.1	46	1.1

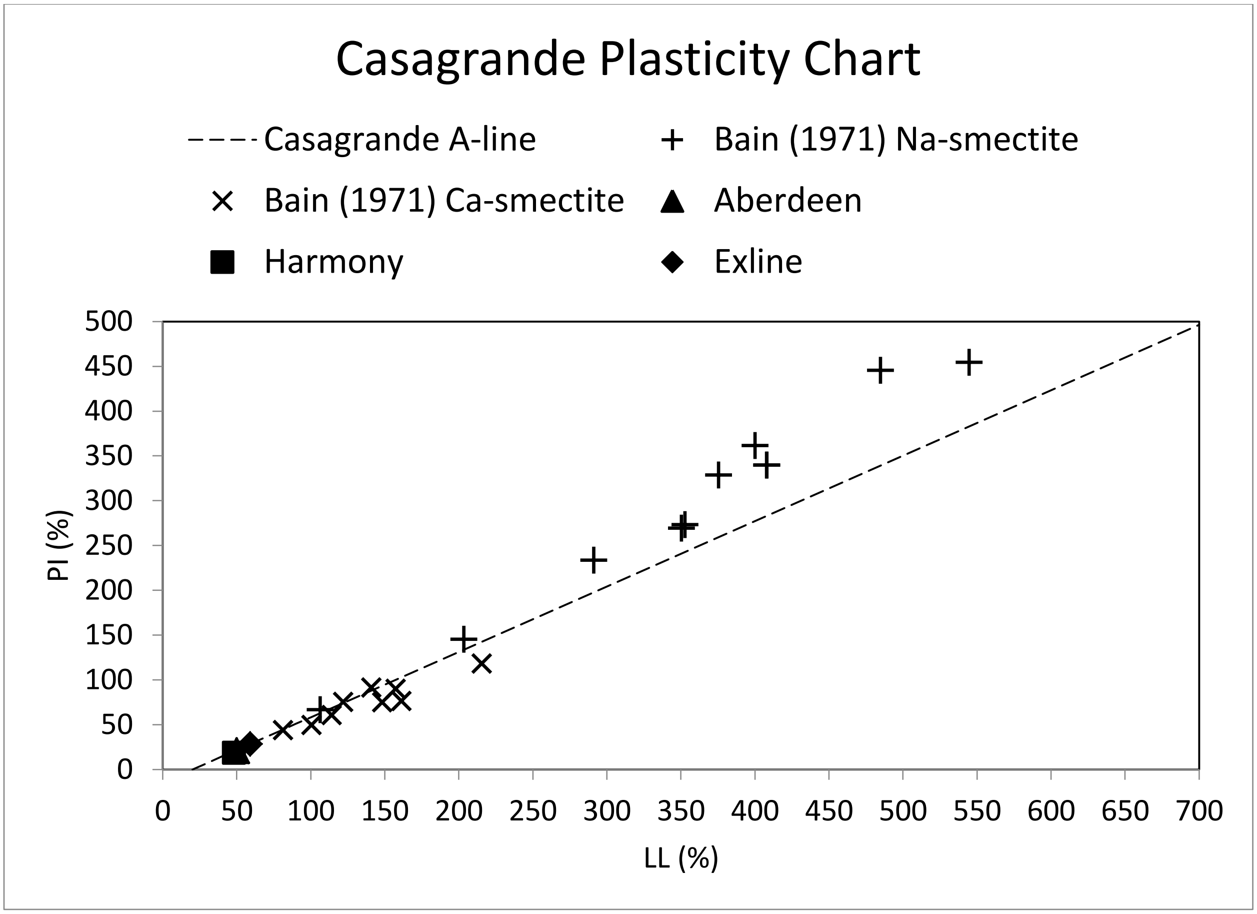

Figure 1. Casagrande plasticity chart for untreated Aberdeen, Exline and Harmony soils, as well as the Na-Smectite and Ca- Smectite from Bain (1971), and the Casagrande A-line (Casagrande, 1932). Liquid limit (LL) and plasticity index (PI).

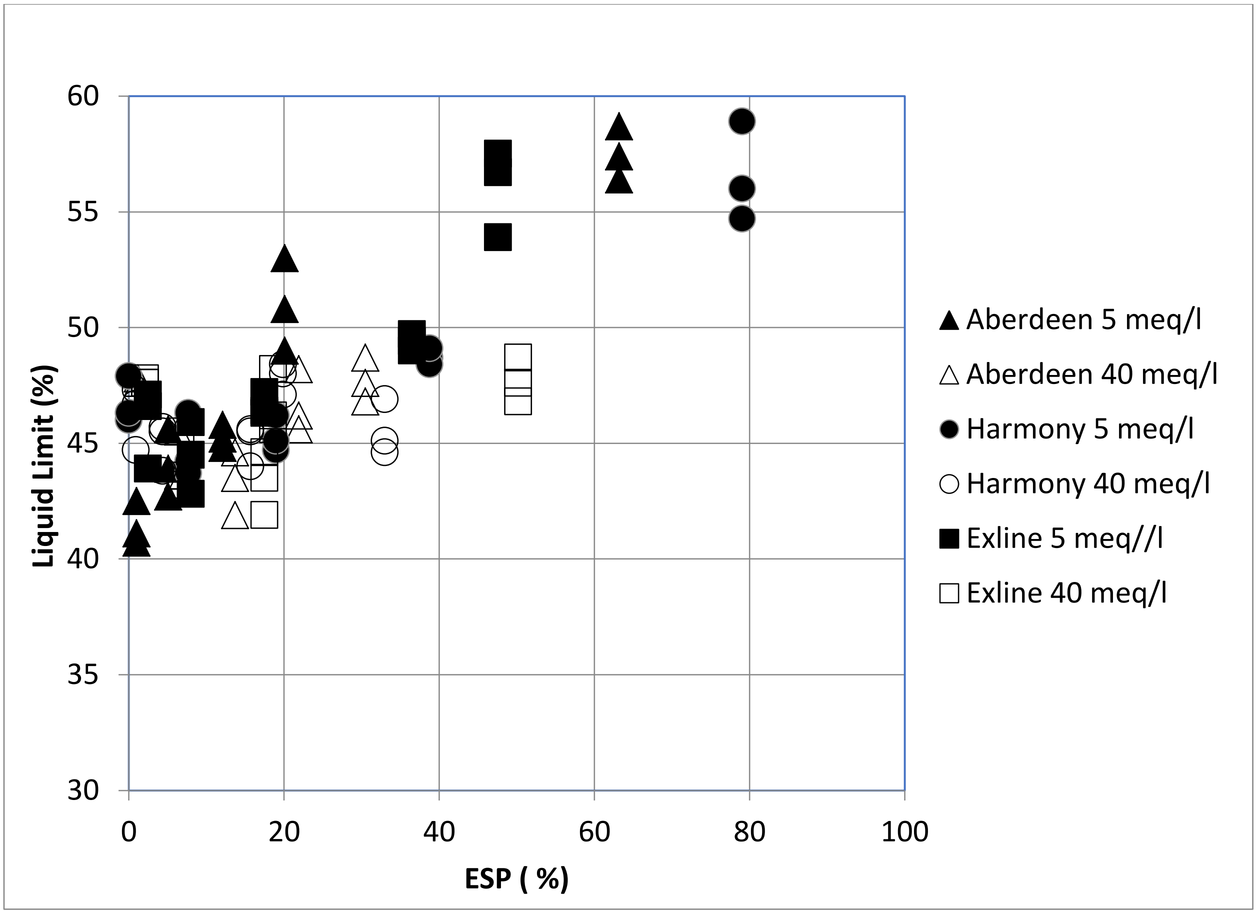

Figure 2. Liquid limit vs. measured exchangeable sodium percentage (ESP) values for Harmony, Aberdeen and Exline soils at salt concentrations of 5 and 40 mmolc dm^{-3}.

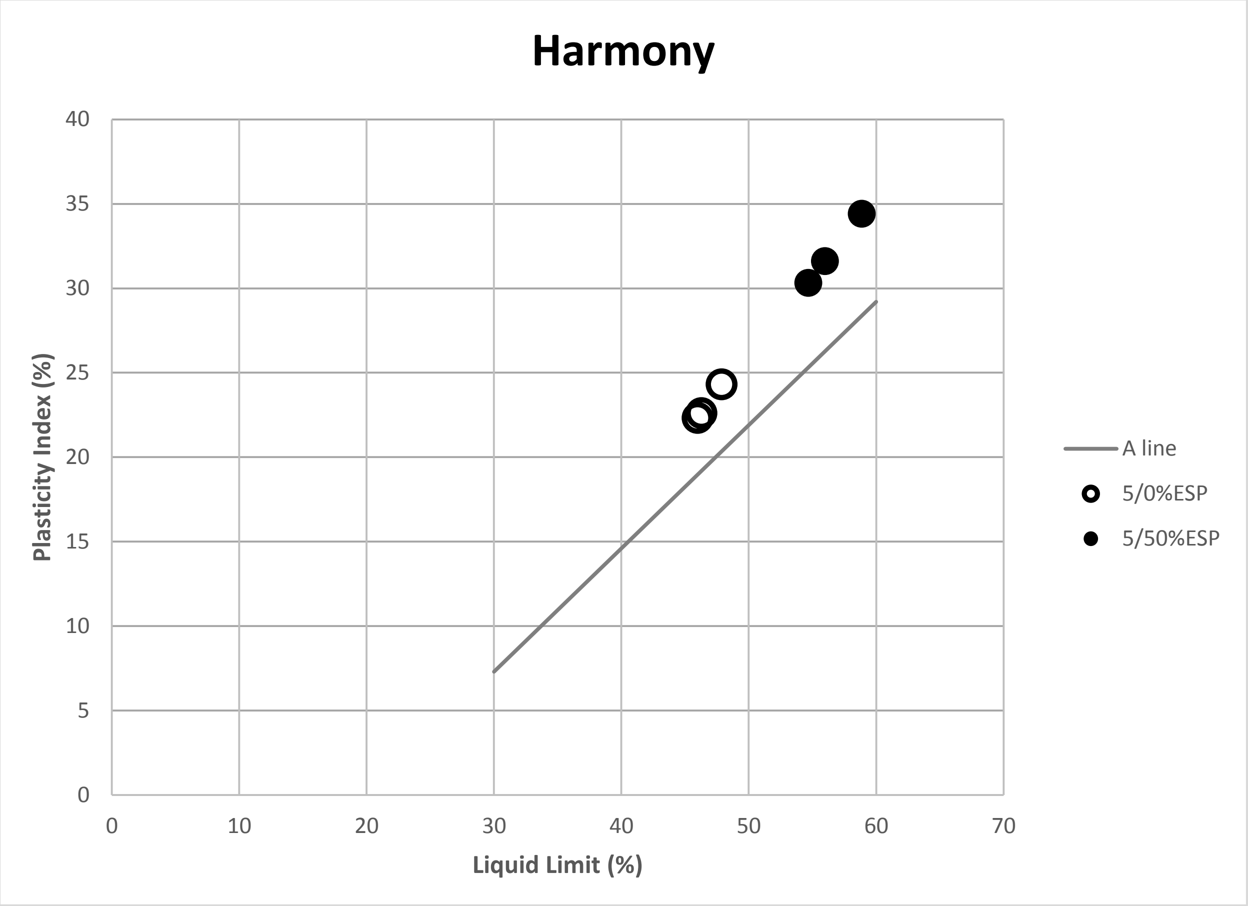

Figure 3. Relationship between liquid limit and plasticity index for Harmony soil with Casagrande A line at 5 mmolc dm^{-3}.

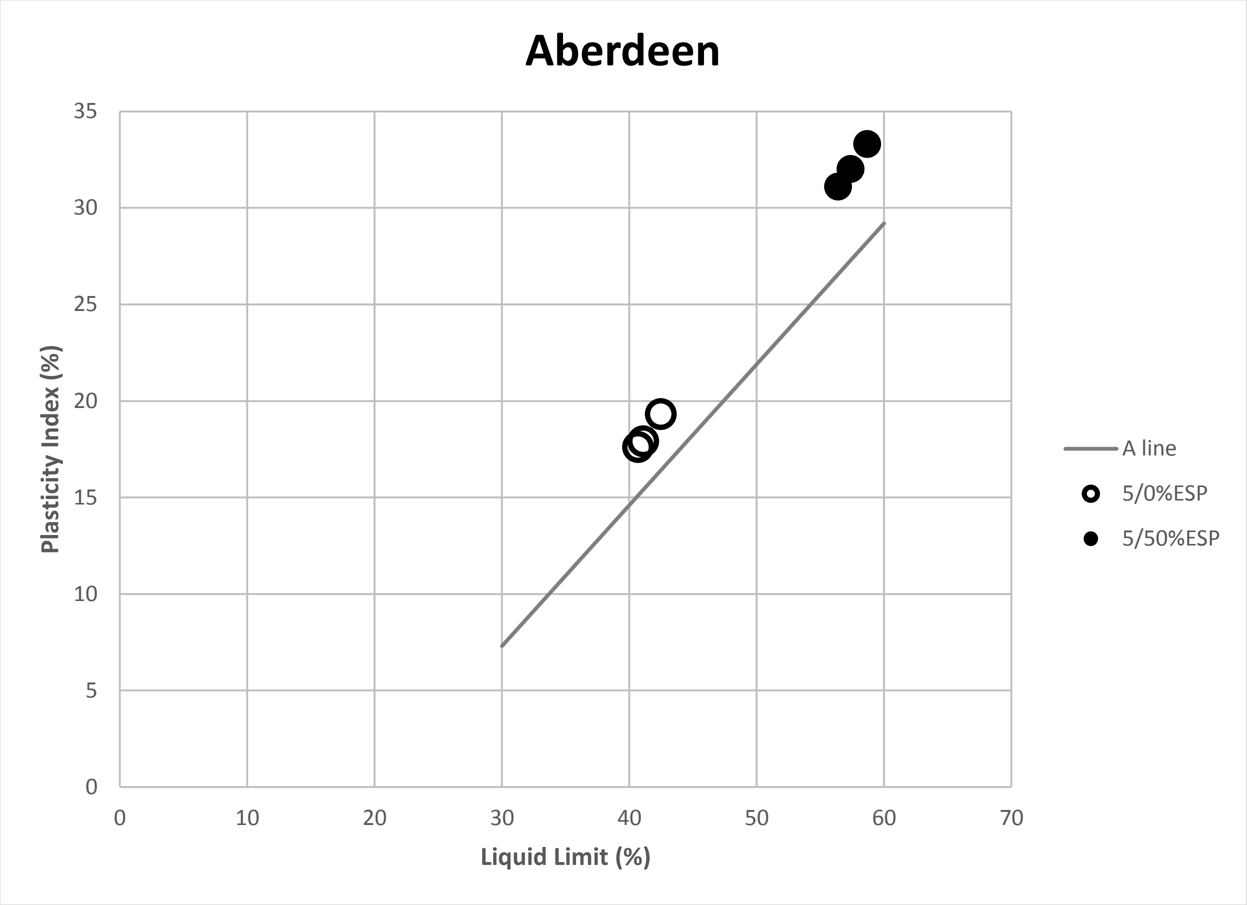

Figure 4. Relationship between liquid limit and plasticity index for Aberdeen soil with Casagrande A line at 5 mmolc dm^{-3}.

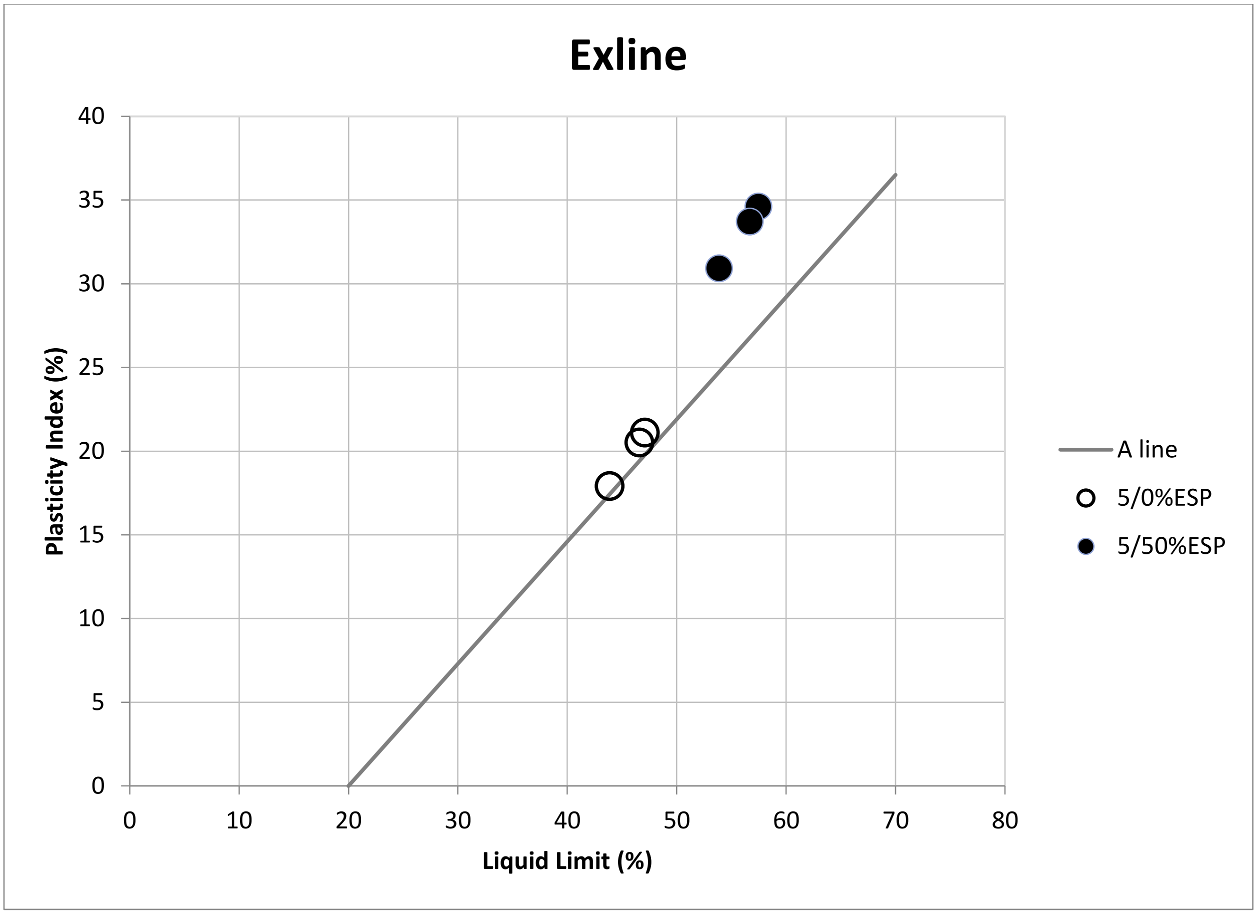

Figure 5. Relationship between liquid limit and plasticity index for Aberdeen soil with Casagrande A line at 5 mmolc dm^{-3}. Low salt low ESP treatment and high ESP treatment are in black circles.

Appendix

Table A.1. Exchange selectivity coefficients for Na^+ /Ca^{2+} Aberdeen, Exline and Harmony soils at salt concentrations of 5 mmolc dm^{-3}, 10 mmolc dm^{-3}, 20 mmolc dm^{-3} and 40 mmolc dm^{-3}. Lower and upper confidence intervals using bootstrap method and RMSE of selectivity coefficient.

Soil	Selectivity Coeficcient	Lower (CI)	Upper (CI)	RMSE
Aberdeen	0.24	0.16	0.35	0.043
Exline	0.44	0.33	0.45	0.027
Harmony	0.19	0.16	0.22	0.015

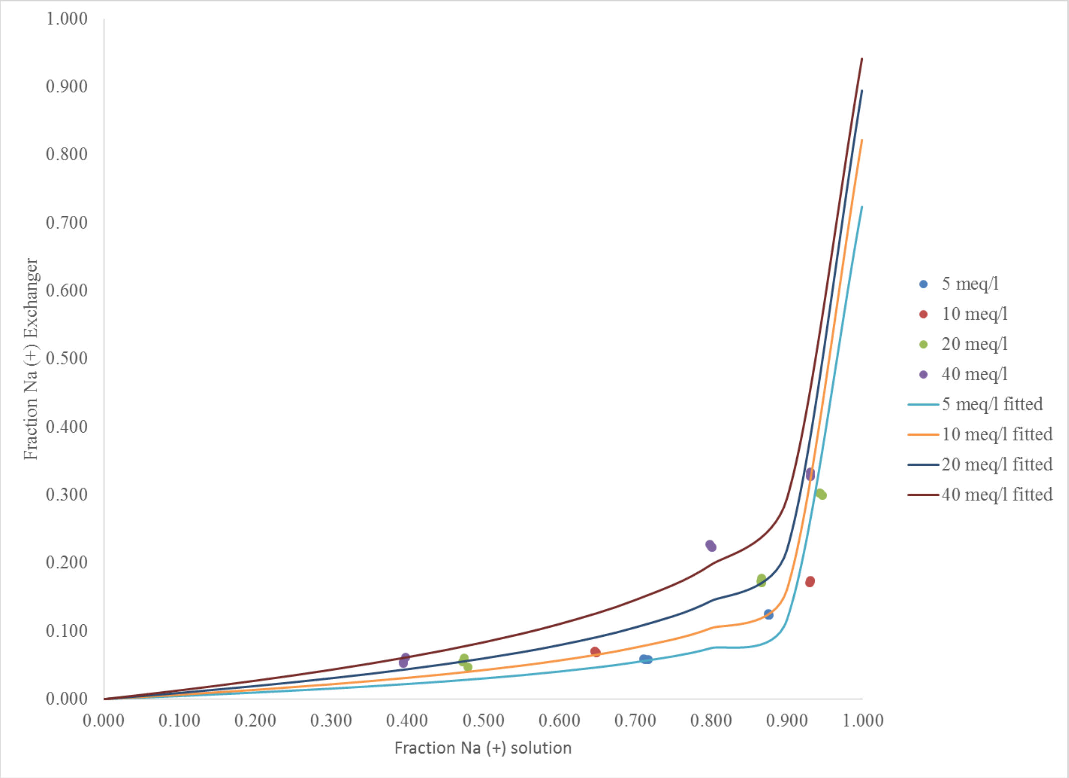

Figure A.1. Harmony Sodium/Calcium exchange isotherm after preliminary solution treatments at 5 mmolc dm^{-3}, 10 mmolc dm^{-3}, 20 mmolc dm^{-3} and 40 mmolc dm^{-3}.

Table A.2 Sodium Carbonate added to make desired exchangeable sodium levels of 6, 15, 25 and 50 % at a salt concentration of 5 mmolc dm^{-3} and 50 % at salt concentration of 10 mmolc dm^{-3}.

Treatment	Aberdeen	Exline	Harmony
5mmolc dm^{-3} ESP 6	1.0	0.900	1.181
5 mmolc dm^{-3} ESP 15	2.833	2.530	3.374
5 mmolc dm^{-3} ESP 25	4.113	4.617	5.520
5 mmolc dm^{-3} ESP 50	9.02	8.012	10.826
10 mmolc dm^{-3} ESP 50	9.242	8.234	11.048

Table A.3 Atterberg plasticity parameters (liquid limit, plastic limit, plasticity index and activity) and coefficient of linear extensibility (COLE) for the Harmony soil in response to salinity and exchangeable sodium treatments.

Treatment	Liquid Limit	Plastic Limit	Plasticity Index	COLE	Clay activity	Cole/ Clay Content
5 mmolc dm^{-3} ESP 0	46.7	23.7	23.1	0.231	0.747	0.747
5 mmolc dm^{-3} ESP 0	46.7	23.7	23.1	0.231	0.747	0.747
5 mmolc dm^{-3} ESP 6	44.7	24.4	20.4	0.204	0.659	0.659
5 mmolc dm^{-3} ESP 15	45.3	24.5	20.9	0.209	0.675	0.675
5 mmolc dm^{-3} ESP 25	48.7	23.6	25.2	0.252	0.815	0.815
5 mmolc dm^{-3} ESP 50	56.5	24.4	32.1	0.321	1.039	1.039
10 mmolc dm^{-3} ESP 0	44.8	24.8	20.0	0.200	0.648	0.648
10 mmolc dm^{-3} ESP 6	45.8	25.7	20.1	0.201	0.650	0.650
10 mmolc dm^{-3} ESP 15	46.0	23.2	22.8	0.228	0.739	0.739
10 mmolc dm^{-3} ESP 25	44.4	22.7	21.7	0.217	0.701	0.701
10 mmolc dm^{-3} ESP 50	53.5	28.9	24.6	0.246	0.796	0.796
20 mmolc dm^{-3} ESP 0	44.0	24.8	19.2	0.192	0.620	0.620
20 mmolc dm^{-3} ESP 6	46.5	22.6	23.9	0.239	0.772	0.772
20 mmolc dm^{-3} ESP 15	46.3	24.3	22.0	0.220	0.713	0.713
20 mmolc dm^{-3} ESP 25	48.6	25.2	23.3	0.233	0.755	0.755
20 mmolc dm^{-3} ESP 50	46.9	25.0	21.9	0.219	0.709	0.709
40 mmolc dm^{-3} ESP 0	46.2	24.6	21.6	0.216	0.699	0.699
40 mmolc dm^{-3} ESP 6	45.0	25.9	19.1	0.191	0.619	0.619
40 mmolc dm^{-3} ESP 15	45.0	24.4	20.7	0.207	0.669	0.669
40 mmolc dm^{-3} ESP 25	47.8	23.4	24.4	0.244	0.791	0.791
40 mmolc dm^{-3} ESP 50	45.5	26.4	19.2	0.192	0.620	0.620

Table A.4 Atterberg plasticity parameters (liquid limit, plastic limit, plasticity index and activity) and coefficient of linear extensibility (COLE) for the Aberdeen soil in response to salinity and exchangeable sodium treatments.

Treatment	Liquid Limit	Plastic Limit	Plasticity Index	COLE	Clay activity	Cole/ Clay Content
5 mmolc dm^{-3} ESP 0	41.4	23.2	18.3	0.184	0.495	0.498
5 mmolc dm^{-3} ESP 6	44.1	21.1	23.0	0.212	0.622	0.575
5 mmolc dm^{-3} ESP 15	45.3	24.3	21.0	0.216	0.568	0.586
5 mmolc dm^{-3} ESP 25	50.9	24.0	26.9	0.275	0.729	0.744
5 mmolc dm^{-3} ESP 50	57.5	25.4	32.1	0.259	0.871	0.703
10 mmolc dm^{-3} ESP 0	43.7	24.1	19.6	0.204	0.531	0.553
10 mmolc dm^{-3} ESP 6	44.0	24.2	19.8	0.190	0.536	0.516
10 mmolc dm^{-3} ESP 15	50.9	22.6	28.3	0.306	0.767	0.830
10 mmolc dm^{-3} ESP 25	47.6	22.0	25.6	0.241	0.693	0.653
10 mmolc dm^{-3} ESP 50	60.7	24.3	36.4	0.288	0.986	0.780
20 mmolc dm^{-3} ESP 0	43.8	23.7	20.1	0.227	0.546	0.616
20 mmolc dm^{-3} ESP 6	44.4	24.0	20.4	0.205	0.553	0.554
20 mmolc dm^{-3} ESP 15	47.5	25.6	21.9	0.245	0.593	0.665
20 mmolc dm^{-3} ESP 25	47	24.0	22.9	0.273	0.621	0.740
20 mmolc dm^{-3} ESP 50	47.8	24.1	23.7	0.235	0.642	0.636
40 mmolc dm^{-3} ESP 0	47.7	21.0	26.6	0.229	0.722	0.620
40 mmolc dm^{-3} ESP 6	44.1	23.2	20.9	0.234	0.567	0.635
40 mmolc dm^{-3} ESP 15	43.3	21.7	21.6	0.251	0.586	0.680
40 mmolc dm^{-3} ESP 25	46.7	24.6	22.1	0.241	0.598	0.652
40 mmolc dm^{-3} ESP 50	47.7	20.6	27.1	0.220	0.734	0.596

Table A.5 Atterberg plasticity parameters (liquid limit, plastic limit, plasticity index and activity) and coefficient of linear extensibility (COLE) for the Exline soil in response to salinity and exchangeable sodium treatments.

Treatment	Liquid Limit	Plastic Limit	Plasticity Index	COLE	Clay activity	Cole/ Clay Content
5 mmolc dm^{-3} ESP 0	45.9	26.0	19.8	0.177	0.559	0.498
5 mmolc dm^{-3} ESP 6	44.4	19.7	24.7	0.222	0.695	0.626
5 mmolc dm^{-3} ESP 15	46.6	24.6	22.0	0.205	0.621	0.578
5 mmolc dm^{-3} ESP 25	49.4	23.6	25.8	0.275	0.726	0.775
5 mmolc dm^{-3} ESP 50	56.0	23.0	33.1	0.313	0.932	0.883
10 mmolc dm^{-3} ESP 0	41.9	21.2	20.7	0.196	0.582	0.551
10 mmolc dm^{-3} ESP 6	40.9	20.6	20.3	0.176	0.572	0.495
10 mmolc dm^{-3} ESP 15	42.2	22.6	19.7	0.186	0.554	0.525
10 mmolc dm^{-3} ESP 25	49.2	25.5	23.7	0.232	0.668	0.653
10 mmolc dm^{-3} ESP 50	52.0	28.7	23.3	0.250	0.655	0.703
20 mmolc dm^{-3} ESP 0	43.5	21.2	22.3	0.188	0.629	0.528
20 mmolc dm^{-3} ESP 6	41.1	23.8	17.2	0.166	0.485	0.466
20 mmolc dm^{-3} ESP 15	42.8	20.5	22.3	0.188	0.627	0.529
20 mmolc dm^{-3} ESP 25	48.0	22.3	25.7	0.259	0.724	0.729
20 mmolc dm^{-3} ESP 50	47.7	22.1	25.6	0.220	0.720	0.619
40 mmolc dm^{-3} ESP 0	45.1	22.2	22.9	0.227	0.645	0.638
40 mmolc dm^{-3} ESP 6	41.7	23.6	18.2	0.194	0.512	0.547
40 mmolc dm^{-3} ESP 15	43.9	21.5	22.4	0.217	0.630	0.610
40 mmolc dm^{-3} ESP 25	48.2	23.0	25.3	0.240	0.712	0.675
40 mmolc dm^{-3} ESP 50	48.0	22.6	25.3	0.230	0.714	0.647

Chapter 2

Determining Changes in Soil Swelling Related Properties From Exchangeable Sodium Percentage

Abstract

The response of soil to irrigation waters with excessive sodium depends on the soil clay behavior. Atterberg limits, soil shrinkage and water release curves are among the soil properties that affect water retention by soil clays, specifically smectite clay minerals. Soil physical properties that can distinguish smectitic soils from non-smectitic soils could identify soils that are sensitive to exchangeable sodium. This study explores the use of Atterberg limits and coefficients of linear extensibility (COLE) as possible properties to determine if a soil is sensitive to exchangeable sodium. Synthetic soils were prepared from mixtures of silt and clay along with 6 natural soils. Water retention, Atterberg limits and soil COLE are also reported for six natural soils at elevated exchangeable sodium percentage (ESP) levels as a comparison. The liquid limit and shrinkage increased as the amount of sodium-saturated smectite increased in the synthetic soils. The liquid limit, shrinkage and water release function at matric potentials greater than -336 cm of H_2O increased on smectite clay dominant soils when elevated ESP was combined with low salinity. The response of soil smectite clays to ESP was similar but to a much lesser degree than on pure smectite clays. There is an increase in the liquid limit by an average of 33 % between ESP 0 treatment and 100% ESP treatment on smectitic soils whereas there was a 253% increase in the liquid limit for synthetic soils prepared from Wyoming bentonite relative to synthetic soils prepared from Fullers earth clay specimens. Smectitic soils had increases in soil swelling related properties whereas non-smectitic clay soils had no changes in swelling related properties from ESP. Results indicate that Atterberg limits and water retention curve points can be beneficial for distinguishing soils that are sodium sensitive. Soils that are smectitic have the greatest increases in swelling and water retention from high ESP requiring careful management of irrigation waters

Introduction

As the worldwide use of water resources is increasing while the supply is decreasing the demand for irrigation waters of sub-par quality (i.e. high salinity and sodicity) is growing (Qadir and Oster, 2003). Many of the procedures used to determine the effects of irrigation waters on soils is time consuming and supply soil-specific results (Qadir and Oster, 2003 and Mc Neal et al., 1966). Soils that contain smectitic clays are known to be most sensitive to low electrical conductivity (EC) and high sodium adsorption ratio waters (SAR) when saturated hydraulic conductivity, soil shrinkage and soil dispersion are measured (He et al., 2015, Malik et al., 1992 and McNeal et al., 1966).Exchange of sodium for calcium favors calcium which makes creating high levels of exchangeable sodium percentage (ESP) while maintaining low EC difficult. Using sodium carbonate to increase ESP of a calcium saturated soil can rapidly increase soil ESP while maintaining low EC (Klopp et al., 2019 and Bain, 1971). Saturated hydraulic conductivity measurements typically report the relative change resulting from the applied solution treatments (McNeal et al., 1966 and Quirk and Schofield, 1955). A rapid soil measurement is needed to distinguish sodium sensitive soils from non-sensitive soils

Sodium smectite shows large increases in swelling at low salinity levels. Swelling, however, decreases as the salinity of the soil solution is increased (Norrish and Quirk, 1954). Sodium smectite is found to exhibit free swelling, whereas sodium-illite and sodium-kaolinite do not show evidence of free swelling at low salinity levels (Seed et al., 1964). Sodium-saturated smectite also has a much greater swelling range compared to a calcium-saturated smectite (Katsumi et al., 2008). McNeal measured swelling of clays extracted from soils in California and found an increase in swelling of the soil clays due to high ESP and low EC (McNeal, 1968). McNeal (1968) did not report whole soil swelling behavior due to high ESP and low salinity levels.

Soil Atterberg limits are a commonly-measured soil property in civil and geological engineering and are used in the Unified Soil Classification System to classify soil texture. (ASTMD2487, 1985). Soil Atterberg limits are an indication of soil strength of 1.7 kPa at the liquid limit and 170 kPa at the plastic limit. This strength indication is where soil changes from a semi solid to a liquid state and where soil changes from a plastic to semi solid state. In soil science particle size analysis is used to classify soil texture and does not take into account the effects of the different clay minerals on soil physiochemical behavior like the Unified Soil Classification System (USCS). Atterberg limits along with particle size distribution determine how USCS classifies soil texture.

Atterberg limits are much higher for sodium-saturated smectite compared to calcium-saturated smectite due to free swelling from water entering the interlayer (Katsumi et al., 2008 and Bain, 1971). Most kaolinite and illite clay specimens contain some smectite giving rise to modest increases in soil liquid limit (LL) under high ESP and low salinity conditions (Shuttlefield et al., 2007). The LL, which is strongly related to free swelling of smectite clay minerals, is a physical measurement related to a certain soil strength value of -1.7 kPa (ASTM D4318, 2017). The plastic limit (PL) is where the soil changes from a plastic to a semi-solid state (ASTM D4318, 2017). Adding sodium carbonate to calcium smectite increases LL values toward the level of sodium smectite due to precipitation of calcium and exchange of sodium for calcium (Bain, 1971). Industrial grade clay minerals can be identified by their Atterberg limits, but little is known how agricultural soils composed of differing clay mineralogy change due to soil sodicity.

Atterberg limits have been measured on whole soils in a few studies. Atterberg limits were found to increase at high ESP and low EC in soils mapped as being smectitic (Klopp et al., in review.). The plasticity index (PI) of soils containing primarily smectite were higher than soils of other clay types in soils from Virginia (Thomas et al., 2000). Soil Atterberg limits were lower in a high ESP and low EC state in an illite clay dominated soil compared to higher EC levels and a calcic state (Lebron et al., 1994). The LL values of the soils used in the Lebron study was lower than reported in other papers (Thomas et al., 2000; Klopp et al., in review).

Soil shrinkage [i.e., coefficient of linear extensibility (COLE)] is another soil property that is dependent on clay types present in the soil (Ross, 1968). The (COLE) is higher in soils that are of smectite mineralogy compared to soils of mica (illite) and kaolinitic mineralogy at given clay content (Thomas et al., 2000 and Ross, 1978). Soil COLE was found to increase as ESP levels increased in smectite dominant soils that are considered to be Vertisols, Mollisols and Aridisols (Klopp et al., 2018 and Malik et al., 1992) .

Water uptake into interlayers of the smectite clay by interlayer cation hydration can alter soil water retention (Lu and Khorshidi, 2015). Soil water content at -336 cm of H_2O was found to increase as ESP increased and EC decreased on a variety of Chernozemic soils (Mollisols) from Saskatchewan and from Mollisols in North Dakota which all had some smectite in their clay mineralogy (He et al., 2015 and Curtain et al., 1994).The water release function of the soil is a measurement of soil water content at a given matric potential, which is dependent upon both the clay mineralogy and structure of a soil. An increase in soil water retention from increasing ESP at low salinity should be directly related to clay swelling.

The degree of swelling exhibited by soil is important for soil hydrologic and mechanical behavior. An increase in clay swelling from ESP may increase water retained by smectite clay and difficulty for salt leaching and soil trafficability. Determining how soil swelling related properties are affected by soil ESP can help to identify soils that have become more plastic and increase in water retention from high ESP.

The first objective of this work was to measure how Atterberg limits and soil shrinkage changes with salinity and ESP for synthetic soil prepared from select clay minerals and silt, and on natural soils of a range of textures and mineralogy; Subsequently, the second objective was to determine how clay swelling affects soil water retention of soils varying texture and mineralogy. The third objective was to identify a soil property that can discriminate soils sensitive to sodicity from soils that are insensitive to sodicity.

Methods

Soils Collected

Three smectitic silty clay loam soils were collected from South Dakota (Aberdeen, Exline and Harmony) from the argillic or natric horizon. Harmony series (Fine, smectitic, frigid Pachic Argiudolls) was collected at 44.9827 N, 98.5088 W from 30-50 cm depth, Aberdeen soil series (Fine, smectitic, frigid Glossic Natrudolls) was collected at 44.9553 N, 98.4426 W from 25-45 cm depth and the Exline soil series (Fine smectitic frigid Leptic Natrudolls) was collected from 44.9550 N, 98.4229 W from 15 to 40 cm depth Argillic horizon from Portwing soil (Fine, mixed, active ,frigid Oxaquic Glossudalf) from Wisconsin and the argillic horizon at 46.837N, 91.08W of a clay textured kaolinitic Cecil (fine kaolinitic, thermic Typic Kanhapludult) Soil from North Carolina from 35.7335 N, 78.6717 W. Fargo soil (Fine, smectitic, frigid Typic Epiaquert) from the A horizon of a silty clay veritsol was collected from North Dakota 47.1729 N,96.9003 W . Particle size analysis of the soils was measured using the pipette method (Deshpande and Telang, 1950). Exchangeable cations were measured using a 1M CsCl extract.

Soluble cations and salinity of the soils were determined using a 1:1 soil: water abstract. Cations present in saturated paste extract, 1:1 extract and CsCl extract were measured using ICP-OES Perkin Elmer Optima 4300 DV. X-ray diffraction was measured on clay fraction by dispersing soil with 50 g/l sodium hexametaphosphate and removing the top 10 cm of liquid after all particles coarser than 2 um were settled out of top 10 cm. After samples were dried and crushed, X-ray diffraction was then measured on the homogenized < 2um fraction.

Synthetic Soils

Silt was purchased from Ward Science (Rochester, NY) and undergone a sedimentation procedure after treatment with sodium hexametaphosphate to remove clay from the soil. After sedimentation was completed, the silt was washed several times with deionized water to remove salinity. The final clay percentage of the silt soil was 1 %. Two representative clay specimens were purchased from Ward's Science (Rochester, NY), with the bentonite from Clay Spur, Wyoming, USA and Kaolinite from Twigg County, Georgia, USA. Fullers Earth was purchased from Sigma Aldrich (St Louis, MO) which was sieved to pass through 100 mesh. Sodium-saturated kaolinite was prepared by treating the clay with 1 M sodium chloride the placed on mechanical shaker for 1 hour and centrifuged with the solution decanted at the end of the centrifuge run. This was done 3 times to saturate with sodium. To reduce the salinity, the solution was decanted from centrifuge tubes, deionized water was then added to the centrifuge tube, shaken for 1 hour, and then centrifuged until the clay would settle out of solution. The solution was decanted and replaced with deionized water. This process was repeated until clay particles remained suspended in solution.

Calcium-saturated kaolinite was prepared by washing with 5 pore volumes of 0.5 M $CaCl_2$ in a column and then was washed with 0.0025 M $CaCl_2$ to reduce salinity; this was continued until the outflow EC was equal to that of the 0.0025 M solution. Calcium-saturated silt was prepared using the same method as was used for the Kaolinite. The treated silt and kaolinite was then air dried and crushed to pass through a 2mm sieve.

The treated silt was mixed with bentonite, Fuller's earth, Ca kaolinite and Na kaolinite to create silt and clay mixes ranging from 20 % of clay mineral specimens to pure clay specimens. Particle size analysis, soluble cations using a 1:1 soil to water extract and exchangeable cations using a 1 M CsCl extract were measured for each specimen. Cations present in the saturated paste extract, 1:1 extract and 1M CsCl extract were measured using ICP-OES Perkin Elmer Optima 4300 DV (Waltham, Massachusetts).

Natural Soil Treatments: Salinity and Exchangeable Sodium

Natural soils were packed in columns and leached with 5 pore volumes of 0.5 M $CaCl_2$ to saturate with calcium. Following this treatment, the influent was changed to 5 mmol l^{-1} $CaCl_2$ solution and leached until outflow EC was equal to inflow EC. The calcium-saturated soils were removed from the columns, air dried and crushed to pass through a 2mm sieve; this constituted the 0% ESP treatment. The 50% and 100% ESP treatments were prepared by adding 50% and 100% of the cation exchange capacity (CEC) as sodium carbonate. For example on Harmony soil 12.6 $cmol_c$ $kgsoil^{-1}$ or 6.68 g $kgsoil^{-1}$ of Na_2CO_3 was used to create the 50 % ESP treatment and 25.2 cmolc $kgsoil^{-1}$ or 13.37 g $kgsoil^{-1}$ of Na_2CO_3 to create the 100 % ESP treatment . Adding sodium carbonate was found to successfully increase the LL and PI of smectite clay specimens by compulsive (Na, Ca) exchange (Bain, 1971). Exchangeable cations, EC and ESP of the samples were measured on the natural soils treated to a range of ESP values. Soil CEC was measured using ammonium acetate pH 7 as measured using sum of cations method on the calcium saturated treatment.

Atterberg Limits and Soil Shrinkage

Atterberg limits were measured on the natural and synthetic soil by wetting with deionized water. LL and PL of the soils were measured using standard methods (Cassagrande, 1932). Samples were treated with the desired sodium carbonate treatment, wetted to close to saturation, and allowed to equilibrate for 24 hours before measurements were made. Synthetic soils were wetted to close to saturation and allowed to equilibrate for 24 hours. Soil shrinkage (COLE) was measured using the rod method on soils and soil mixes wetted with deionized water until they formed to the consistency of a saturated paste (Schaffer and Singer, 1976).

Water Retention

Natural soil specimens from the ESP 0%, ESP 50% and ESP 100% treatments were packed into round cores 2.5 cm high and 5 cm in diameter with the same mass of the soil packed into each core. The soil cores were packed in a uniform way to a bulk density of 1.15 g cm^{-3}. Samples were wetted with deionized water for 72 hours. The samples were then placed on a tension table and equilibrated to a pressure of –102 cm of H_2O. The same samples were transferred to a pressure plate and equilibrated to -336 cm of H_2O pressure. At the end of the pressure plate run samples were air dried at 105 degrees C to determine oven dry soil mass of the sample.

Statistical Analysis

The relationship of plasticity index vs ESP for the soils and the relationship of plasticity index vs clay content for the synthetic soils were explored with a linear regression. Pooled standard deviation was calculated on the liquid limit, plasticity index, COLE and water retention at three potentials to determine the relative change between the individual ESP treatments for a given soil. The Cohen d statistic (Cohen, 1988) was used to quantify the effect size for each soil property caused by increasing ESP at low salinity. Pedotransfer functions were developed to predict the LL, PI , coefficient of linear expansion (COLE) , and soil water content at -336 cm of H_2O ($w_{1/3}$) using a random 75% of the data of natural soils combined data with data from Chapters 1 and 3. The functions were verified on 25 % of the random data from this study and with Atterberg limit data and water retention from soils of natric great groups in the National Cooperative Soil Survey database (National Cooperative Soil Survey). The prediction data set had 174 samples, verification had 58 and the soil survey characterization data had 291 samples when combining all horizons from sodic soils. The root mean square error (RMSE) and bias of the prediction equation were calculated to determine the performance of the prediction equation.

Results

X-ray diffraction

The clay fraction of the Aberdeen, Exline, Fargo and Harmony soils were mostly smectite and illite with small amounts of kaolinite and quartz in the samples. The Portwing soils clay fraction was primarily illite with small amounts of smectite, kaolinite, hematite and quartz, whereas the Cecil soils clay fraction was primarily kaolinite with small amounts of hematite, gibbsite and quartz within the soil. The X-ray diffraction of the clay mixes was conducted using the same procedure as the natural soils except no sedimentation procedure to remove clay fraction. The bentonite soil contained primarily montmorillonite with a trace of quartz, the Kaolinite was mostly kaolinite and the Fullers Earth was primarily palygorskyte, and smectite, with small amounts of quartz, dolomite, and calcite in the sample

Atterberg Limits and Plasticity

The LL and PI were vastly different for ESP effect on synthetic soils prepared by mixing clay mineral specimens and silt together in different percentages (Figure 1). A Casagrande plasticity chart reveals synthetic soils prepared with bentonite (nominally Na-saturated smectite) had much larger LL and PI regardless of clay percent compared to the other clay minerals (Figure 2). Soils containing a greater percentage of bentonite in soil clay mix plotted a further distance above the A line (Figure 2). The A line is a line that passes through a plot of liquid limit vs plasticity graph that is used to separate clays from silts (ASTM4312).

The USDA soil classifications of the synthetic soils ranged between loam and clay with most of the silt clay mixes consisting of loam or clay texture (Table 2). The USCS textural classifications of the same synthetic soils consisted of a wide variety of soil classes based upon clay behavior and particle sizes within the samples (Table 2). Increasing the amount of bentonite in the sample took synthetic soils from below the Casagrande A line to above the A line (Figure 2). If the sample is below the A line it behaves like low-plasticity silt and if it's above the A line the soil is high-plasticity clay. USCS classification of the soils ranged from a sandy silt to a CH "fat clay"[3] (Table 2).

The slope of the line of the relationship between Atterberg limits and clay percentage (Figure 1) increased as bentonite or Fuller's earth percentage of the sample increased. The bentonite and Fuller's earth had a strong relationship between plasticity index and clay content (Table 4). The bentonite had a slope of PI vs clay content of 8.7 whereas sodium kaolinite had a slope of 0.164. Increasing the amount of bentonite or Fuller's earth in the sample increased the slope of the regression lines (Table 4). Bentonite percentage in the synthetic soils was the

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[3] The USCS terms "lean" and "fat" relate to low and high liquid limits, a measure of plasticity. Above the Casagrande A-line a CL or "lean" clay has relatively low plasticity while a CH or "fat" clay has relatively high plasticity. Below the Casagrande A-line a ML or "lean" silt has relatively low plasticity while a MH or "fat" silt has relatively high plasticity.

dominant factor in increasing the liquid limit and plasticity index with a strong linear relationship.

Atterberg limits of calcium saturated whole soils did not separate out by their clay activity (PI/clay content) (Figure 4). Soils that were classified as smectitic had increases in soil LL with addition of sodium carbonate. The Portwing and Cecil soils had a small decrease in soil LL with increases in soil ESP.

Coefficient of Linear Extensibility

COLE vs clay content showed a linear relationship for the synthetic soils composed of silt plus Fuller's earth and silt plus bentonite (Figure 3). Sodium and calcium kaolinite had a weak relationship between clay content and soil COLE (Table 5). The COLE values of the kaolinite mixes were significantly lower when compared to the mixes containing smectite specimens. Shrinkage of samples was dependent upon expandable clay content within the mixture.

Soil COLE also had large changes when converting smectitc soils from a sodium state to a calcium state. Soil COLE increased with ESP in soils that contained a moderate to high amount of smectite (Figure 5). Soil COLE did not have any major differences in Portwing soil and had a decrease in the Cecil soil. Soil COLE had less of a difference between treatments compared to soil LL (Table 6).

Water Retention

Water retention increased at low matric potentials for natural smectitic soils as ESP increased. The soils that contained high amounts of smectite clay minerals had large increases in water retention as ESP increased (Figure 7 and Table 2). The Cecil and Portwing soils had a smaller increase in water retention with ESP but the increase still was significant. The samples at 100 % ESP may have had a greater amount of sodium carbonate that remained in solution causing salinity masking the effect of ESP.

Soil Response to Exchangeable Sodium: Significance and Effect Size

Effect size using pooled standard deviation was done comparing the 5 meq /l ESP 0% treatment to the ESP 50% and ESP 100% treatments. The soil COLE had the smallest differences in the measurements that were compared although many of the effects were still large (Table 6). The soils that are classified as smectitic and were found to consist of smectite and illite clays consistently had large increases in Atterberg limits, water retention and soil COLE. The water retention at -102 cm of H_2O and -336 cm of H_2O had the largest effect size of the soil measurements that were conducted.

Pedotransfer Functions

The pedotransfer functions to best predict soil liquid limit was created by combining the liquid limit data from (Klopp et al., in review) and from the national soil survey characterization data. . The Atterberg limits, COLE and $w_{1/3}$ were predicted using the properties of EC, ESP, SAR, Cation Exchange Capacity pH_7 (CEC) and clay percentage. CEC had a larger influence in the soil properties than clay content (Tables 7-10). The LL was predicted using EC, ESP clay and CEC with a RMSE of 9.66 % and a bias of -0.16 on all data with a R^2 of 0.66 on the verification data but a R^2 of 0.33 on the soil survey data (Table 7). The best equation to predict PI also used the same inputs soil properties as the equation to predict soil liquid limit which predicted PI with a RMSE of 5.7 and 8.5% and R^2 of 0.51 and 0.16 respectively on the 2 datasets of verification data and from soil survey (Table 8). The equation to predict $w_{1/3}$ water content had a RMSE of

0.041 and 0.182 g g^{-1} and a R^2 of 0.88 and 0.024 respectively on the verification data and the soil survey data (Table 9). The soil COLE was predicted using the same input factors with an RMSE of 0.033 and a R^2 of 0.60 (Table 10). The R^2 was between 0.5 and 0.7 between the $w_{1/3}$ water content, COLE, LL and PI (Tables 7-10). The soil survey data did not correlate to changes in soil EC by ESP combination, as was found in the verification data used from this study. The $w_{1/3}$ water content was the most strongly correlated physical property to soil solution, in combination with soil clay percentage and CEC. The predicted vs fitted graphs show that data is normally distributed on both sides of the 1 to1 line (Figure 7).

Discussion

The bentonite had a much greater LL than the Fuller's earth or kaolinite. The kaolinite had a slight decrease in LL when it went from being calcium saturated to sodium saturated. The Fuller's earths LL and PI was like other values found on Fuller's earth specimens although this contained some palygorskite in its clay fraction. (Galan, 1996 and Bain, 1971). Calcium kaolinite had a similar LL value to other pure kaolinite specimens (Schmitz et al., 2004). Other studies also have found much greater plasticity index in sodium smectite compared to the Fuller's earth and the kaolinite specimens (Katsumi et al., 2008 and Bain, 1971). The swelling of samples was directly dependent on the amount of bentonite or fullers earth clay in the sample. If you divided the plasticity index by percent bentonite in the 10% bentonite, 10% Na kaolinite and 80% silt the plasticity index was approximately 70 which is 10 times bentonite clay activity of 7.

The relationship between percentage clay and plasticity index was much higher for bentonite compared to the Fuller's earth or the sodium and calcium kaolinites. In a study mixing kaolinite and bentonites with silica sand, Polidori (2007) found a linear increase with a y-intercept through 0 as was found in this study. Soil clay activity, which is PI/clay percentage, are like the regression values found in previous studies (Polidori 2007 and Skempton 1953). Using mixes of these clay-silt specimens supports the hypothesis put forth by McNeal that the smectite fraction of the soil behaves as Wyoming bentonite. The following discussion will show that this assumption is not reasonable.

The USCS classification changed when LL on some soils increased from ESP, indicating solution composition can change certain soil physical properties. The smectitic soils went from behaving like lean (low plasticity) clay or silt to behaving like fat (high plasticity) clay. The synthetic soils composed of 20 % bentonite and 80 % silt, 20 % Na kaolinite and 80 % silt, and 10 % bentonite 10 % Na kaolinite and 80 % silt are all loam texture under USDA classification but the plastic behavior of clays cause them to be very different from each other. The synthetic soils containing Na kaolinite behave as sandy lean (low plasticity) clay whereas the synthetic soils prepared with bentonite behave like a sandy fat clay. Interlayer water uptake and the plasticity of clay minerals, not just particle size distribution, change water behavior in the soil.

In a study measuring Atterberg limits in soils that were identified as montmorillonite dominant soils from India (Sridharan et al., 1986), clay activities ranged between 0.65 and 2.58 with the ESP of these soils all being 22 percent or lower. This study also found an increase in soil LL vs. ESP although the percent clay and specific surface area of these soils varied. In a different study measuring the LL of kaolinite dominated soils (Sridharan et al., 1988), the clay activity values ranged between 0.44 and 1.69. The range in clay activity is much greater than what was found in this study using synthetic soils prepared from pure kaolinite clay specimen. The CEC and specific surface area of the Sridharan soils was greater than the kaolinite specimens used in this study (Sridharan et al., 1988).

Assuming that all of the clay identified in the natural soils as smectite by X-ray diffraction would behave like an ESP 50% or ESP 100% smectite, it would be expected that the Aberdeen, Fargo, Exline and Harmony soils to have clay activities much greater than those found in this work. For soils to be classified as smectitic there is a requirement of 40 % of the clay fraction to be smectitic (National Cooperative Soil Survey Staff 2014). In this case the Harmony soil which is 30% clay should have a minimum plasticity index of 104.4 in the 100% Na treatment if clay was behaving as a Wyoming bentonite specimen. The clay activity of the Harmony 100% Na soil was closer to values from illite clays (Skempton, 1953). Considering the previous studies that have measured X-ray diffraction on soils and Atterberg limits and this study neither the kaolinitic soils behave as pure kaolin clay and the soils that are smectitic do not behave necessarily as a Fuller’s earth or a bentonite. Assuming the soil smectite with a high ESP behaves as a Wyoming bentonite (McNeal et al., 1966) is unfounded.

Soil COLE increased linearly with clay percentage for synthetic soils prepared from bentonite and Fuller’s earth with synthetic soils prepared from Na and Ca kaolinites increasing at a much lower rate. As the percent clay in the sample increased, the COLE/ %clay ratio decreased. This indicates the importance of soil clay type and amount on the soil fabric on behavior. An increase in shrinkage and a decrease in COLE/divided by clay content as clay content increased was found on a mixture of Leda Clay and glass beads also (DeJong and Warkentin, 1965). Kaolinite is incapable of macroscopic swelling occurring, but the volume of the kaolinite clearly changes when it is wetted (Tessier and Pedro, 1980). The kaolinite simply has a change in volume from its initial wetted state to its dried state in which none of the volume change is due to swelling of the kaolinite clay. It is also possible some of the volume change results from swelling clay mineral impurities within certain kaolinite sample.

The soils with expandable clay minerals increased in COLE when treated with sodium carbonate, whereas the soils with low amounts of expandable minerals did not change or decreased in COLE when they underwent a sodium carbonate treatment. Soil shrinkage increased with ESP on smectitic soils as was found in other studies on smectite dominant soils (Klopp et al., 2019 and Malik et al., 1992) The COLE of all the treated soils plotted between the sodium kaolinite values and the Fuller's earth values regardless of the ESP value, which is further evidence that soil smectites do not swell as much as Wyoming bentonite.

Comparing Atterberg limits and shrinkage of pure clay mineral specimens to natural soils led to a reduced change in swelling when comparing pure soils to clay minerals. The soils that were at least half smectite by XRD intensity had a much lower degree of shrinkage and water uptake compared to pure clay minerals. If uptake of water was due to the domain model as proposed by (McNeal et al., 1966) there would be a much larger increase in soil LL and soil shrinkage under high ESP. The uptake of water by soils and shrinkage clearly differed by whether the soil had an abundance of smectite or little smectite in the soil. The soils with low amounts of smectite had no increase in LL or COLE when the soil was treated with sodium carbonate, whereas the smectite abundant soils increased in COLE and LL.

Water retention at -336 cm of H_2O matric potential can also be used as an indication of soil swelling. Soil water retention increased in the smectitic and illite clay dominant soils as exchangeable sodium percentage increased as was found in other studies conducted on smectitic soils (He et al., 2014 and Curtain et al., 1994). Water retention had the largest relative increase in the smectitic soil with the highest clay content as would be expected from free swelling of smectite clays from exchangeable sodium The amount of water intake did not increase much further between the ESP 50% and ESP 100% treatments.

The three soil swelling related properties measured in this study agreed well with each other in trends vs ESP but were poor at predicting the properties on characterization data. The soil survey manual recommends using 0.005 M calcium sulfate solution when measuring water retention specifically on swelling soils due to dispersion of clays and cites ASTM 4312, but does not give a recommendation of wetting solution for the wetting solution for Atterberg limits. (Soil Survey Staff, 2014). ASTM 4312 recommends using deionized water for washing and measurement of Atterberg limits due to the effects of solution composition on soil Atterberg limits. Using calcium sulfate or tap water masks the effect of ESP on soil water retention or Atterberg limits. If the effects of solution composition on soil properties careful consideration of wetting solution needs to be taken to get desirable results.

Effect size comparing the ESP 50% treatment and ESP 100% treatments to the calcic ESP 0% treatment showed a huge difference in changes between the smectitic soils and the Portwing and Cecil soils. The smectitic soils had large increases in the LL values whereas the other soils had no change or decreases in their LL values as soil ESP was increased. The water retention increased with ESP in the smectitc soils and the illitic Portwing soil that has a small amount of smectite in the clay fraction (Figure 6). The soil water content at -102 cm and at –336 cm H_2O was better indicators of free-swelling from soil smectites than the saturated water content. The -1/10th and -1/3rd cm water contents are often reported in soil survey characterization data along with whole soil Atterberg limits making them a suitable indicator of smectite clay presence in soils. Using effect size can separate soils that contain smectite from soils that do not contain smectite.

Conclusions

Soil Atterberg Limits and COLE are properties that measure water uptake of the soil and volume change due to water behavior in the soils. Whole soil LL and COLE increased linearly with sodium smectite in the synthetic soils. Natural soils containing smectite clay had much lower LL and shrinkage compared to synthetic soils prepared from pure sodium-saturated smectite (i.e., bentonite). The soils that contained smectite had much less water uptake compared to the Wyoming bentonite when treated to high exchangeable sodium percentage. The clay type within the soils and the total amount of clay total are both important for water uptake by soils clay fraction. Soil smectites do not behave like a Wyoming bentonite as their exchangeable sodium percentage increases.

Soil physical properties related to swelling of soil clays can be used to discriminate soils that are highly sensitive to exchangeable sodium from soils that are not sensitive to exchangeable sodium. It comes as no surprise that soils that are smectitic show large increases in LL and soil water retention however, soil smectites are consistently less active than the pure smectite specimens collected from geologic formations. This study found a simple soil test that quantifies changes in whole-soil Atterberg liquid limits or water retention at field capacity from calcium saturated soil to soil treated with sodium carbonate to increase ESP while maintaining low salinity. This approach can identify soils that contain moderate to high amounts of smectite in the soil clay fraction without recourse to X-ray diffraction or uncertainties caused by the lower clay activity typical of soil smectite clay minerals. Swelling based properties are strongly related to each other and the cation exchange capacity of the soil.

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Tables and Figures

Table 1 . Sand, silt, clay, cation exchange capacity (CEC), Exchangeable sodium percentage (ESP) , Electrical Conductivity (EC), USDA Soil Classification and USCS Soil Classification for soil specimens used in this study.

Soil	Sand (%)	Silt (%)	Clay (%)	CEC cmol kg^{-1}	ESP (%)	EC (dS m^{-1})	USDA Classification	USCS Classification
Aberdeen	1.90	61.2	36.9	21.1	11.4	0.660	Silty Clay Loam	Fat Clay
Cecil	24.3	25.7	50.0	4.56	1.7	0.624	Clay	Fat Clay With Sand
Exline	3.10	61.4	35.5	18.7	37.0	3.15	Silty Clay Loam	Elastic Silt
Fargo	1.6	48.5	49.9	24.5	0.001	0.489	Silty Clay	Elastic Silt
Harmony	10.1	59.0	30.9	25.4	0.967	0.590	Silty Clay Loam	Silt
Portwing	30.9	44.4	24.7	7.60	0.00	0.370	Loam	Sandy Lean Clay

Table 2. Soil mix, sand ,silt and clay percentage, Cation Exchange Capacity (CEC), Exchangeable Sodium Percentage (ESP) Electrical Conductivity (EC), USCS soil classification with Fat Clay (FC), Lean Clay (LC),Sandy Fat Clay (SFC), Sandy Lean Clay (SLC) , Silt(S) Elastic silt (ES), Sandy Elastic Silt (SES) and Sandy silt (SS) and USDA Soil Classification with Clay (C), Silty clay (SC). Loam (L) and Clay loam (CL) for mixed soil specimens used in this study.

Soil Mix	Sand (%)	Silt (%)	Clay (%)	CEC (cmol+ kg^{-1})	ESP (%)	EC (dS m^{-1})	USCS	USDA
Bentonite	1.90	27.1	71.0	62.8	64.2	1.58 (1:5)	FC	C
Fullers earth	4.40	46.9	48.7	58.2	0.003	0.625	ES	SC
Kaolinite	0.003	30.2	69.8	4.56	1.70	0.221	ES	C
20 % bentonite 80% silt	42.3	44.5	13.2	24.7	70.60	2.56	SFC	L
40 % bentonite 60 % silt	23.5	49.2	27.3	41.5	77	2.68	FCS	CL
20% fullers earth 80 % silt	49	40	11	10.8	0	0.726	SES	L
40% fullers earth 60 % silt	35.6	43.3	21.1	36.4	0.12	0.561	SES	L
20 % sodium kaolinite 80% Silt	46.6	36.7	16.7	7.1	90.0	1.37	SLC	L
40 % sodium kaolinite 60% Silt	35.5	21.2	33.3	3.2	71.6	0.533	SS	CL
sodium kaolinite	0.03	30.2	69.8	8.53	86.3	0.634	S	C
20 % calcium kaolinite 80% Silt	46.6	36.7	16.7	7.4	0.80	0.473	SS	L
40 % calcium kaolinite 60% Silt	35.5	21.2	33.3	11.6	1.10	0.445	SS	CL
calcium kaolinite	0.003	30.2	69.8	5.64	0	0.516	ES	C
10 % bentonite 10 % fullers earth 80 % silt	47.0	41	12.0	22.1	55.5	1.64	SFC	L
20 % bentonite 20 % fullers earth 60 % silt	36.4	39.7	23.9	35.7	65.7	1.54	SFC	L
50 % bentonite 50 % fullers earth	3.15	37.1	59.8	60.59	50.4	1.10	FC	C

5 % bentonite 5 % fullers earth 5 % sodium kaolinite 5 % calcium kaolinite 80 % silt	47.2	39.8	13.0	20.9	64.1	0.846	SES	L
10 % bentonite 10 % fullers earth 10 % sodium kaolinite 10 % calcium kaolinite 60 % silt	35.8	38.3	25.93	19.6	37.9	1.04	SFC	L
25 % bentonite 25 % fullers earth 25% sodium kaolinite 25 % calcium kaolinite	1.58	33.4	65	35.7	46.4	0.243	FC	C
10% bentonite 10% sodium kaolinite 80 % silt	47.1	38.8	14.1	22.1	82.2	1.06	SFC	L
20% bentonite 20% sodium kaolinite 60 % silt	35.4	36.4	28.2	18.7	79.7	2.04	SFC	CL
50 % Bentonite 50 % sodium kaolinite	0.95	28.6	70.5	35.7	75.3	1.01	FC	C
10% Fullers Earth 10% calcium kaolinite 80 % silt	47.3	40.8	11.9	13.4	1.73	0.468	SS	L
20% Fullers Earth 20% calcium kaolinite 60 % Silt	36.1	40.2	23.7	11.6	0.01	0.508	SES	L
50 % Fullers Earth 50 % calcium kaolinite	2.2	32.6	65.2	33.1	0.188	0.186	ES	C
10 % sodium kaolinite 10 % calcium kaolinite 80 % silt	46.6	36.7	16.7	9.11	29.11	1.16	SS	L
20 % sodium kaolinite 20 % calcium kaolinite 60 % silt	35.5	21.2	33.3	8.69	32.6	0.719	SLC	L
50 % sodium kaolinite 50 % calcium kaolinite	0.003	30.2	69.8	5.45	36.0	1.09	LC	C

Table 3. Effects of the solution treatments on the soil specimens used in this study. Soil Treatment, Electrical Conductivity (EC), Exchangeable Sodium Percentage (ESP), Liquid Limit (LL) Plasticity Index (PI), coeficcient of linear expansion (COLE), 1/10th bar water content , 1/3rd bar water content and USCS soil classification with Silt (S), Elastic Silt (ES), Fat Clay (FC), Lean Clay (LC), Fat Clay with Sand (FCS), Lean Clay with sand (LCS) and Sandy lean clay (LCS) are the column titles

Soil treatment	EC (dSm^{-1})	ESP (%)	LL (%)	PI (%)	COLE (mm mm^{-1})	1/10 th bar (%)	1/3rd bar (%)	USCS
Aberdeen 0% Na	0.337	1.00	41.5	18.3	0.184	45.3	37.8	S
Aberdeen 50% Na	0.585	37.4	55.2	19.9	0.185	74.4	66.3	ES
Aberdeen 100 % Na	0.971	81.1	58.0	33.8	0.271	70.5	64.5	FC
Cecil 0% Na	0.576	0	56.1	27.5	0.254	45.0	34.1	FCS
Cecil 50% Na	0.909	62.3	45.6	21.6	0.129	43.8	36.9	LCS
Cecil 100% Na	1.64	76.1	51.8	25.6	0.138	41.6	35.9	FCS
Exline 0% Na	0.471	2.50	45.9	19.9	0.177	44.9	36.9	LC
Exline 50% Na	0.602	47.0	53.6	29.5	0.218	64.0	53.6	FC
Exline 100% Na	0.701	82.5	60.2	26.7	0.305	66.0	57.4	ES
Fargo 0% Na	0.500	0	62.9	28.5	0.280	49.9	43.8	ES
Fargo 50 % Na	1.00	61.3	81.2	47.3	0.356	97.8	83.8	FC
Fargo 100% Na	1.59	83.6	81.2	47.3	0.365	95.4	86.9	FC
Harmony 0% Na	0.580	00	46.7	23.1	0.167	43.4	34.6	LC
Harmony 50 % Na	0.861	37.8	56.5	28.3	0.222	73.1	67.7	FC
Harmony 100% Na	1.22	70.5	61.6	34.9	0.262	75.5	70.6	FC
Portwing 0% Na	0.186	0.00	35.4	19.2	0.153	30.2	23.1	SLC
Portwing 50 % Na	0.805	52.2	26.1	9.2	0.135	35.6	30.8	SLC
Portwing 100% Na	1.26	91.7	26.3	11.0	0.141	34.6	30.7	SLC

Table 4. The Y intercept, slope and R^2 of ESP vs plasticity index for 0% ESP, 50% ESP and 100 % ESP treatments using a linear regression model for each of the natural soil specimens

Soil	Y intercept	Slope	R^2
Aberdeen	16.1	0.197	0.818
Cecil	25.8	-0.0247	0.043
Exline	16.31	0.403	0.9096
Fargo	29.3	0.24	0.898
Harmony	22.7	0.167	0.632
Portwing	17.6	-0.095	0.572

Table 5. Linear regression equations fit to clay percentage vs PI and COLE for the soil specimens used in this study. Mixes of certain ratio of clays, Slope of clay percentage vs plasticity index (Slope PI), R^2, Slope of COLE vs clay content (Slope COLE) and R^2 of equation are the column titles. The Y intercept was set at 0.

Clay Mix	Slope PI	R^2 PI	Slope COLE	R^2
Na Smectite	8.70	0.993	0.0177	0.85
Ca Smectite	2.18	0.942	0.0103	0.800
Na Kaolinite	0.164	0.887	0.0017	0
Ca Kaolinite	0.329	0.993	0.0032	0.4023
50 % Ca Smectite 50 % Na Smectite	4.95	0.966	0.0129	0.788
50% Ca Smectite 50% Ca Kaolinite	0.829	0.978	0.0057	0
50 % Na Kaolinite 50 % Na Smectite	3.27	0.990	0.00095	0
50 % Na Kaolinite 50 % Ca Kaolinite	0.1039	0.978	0.0028	0
25% Na Smectite 25 % Ca Smectite 25 % Na Kaolinite 25% Ca Kaolinite	1.92	0.987	0.0061	0.175

Table 6. The Power analysis effect size for the Aberdeen, Cecil, Exline, Fargo, Harmony and Portwing soil's Liquid Limit, COLE, and Water Retention at saturated water content, -102 cm and -336 cm of H_2O water content. The comparisons are between the ESP 0% and ESP 50% treatments and the ESP 0% and ESP 100% treatment.

Soil	Aberdeen	Cecil	Exline	Fargo	Harmony	Portwing
Liquid Limit						
ESP 0% ESP 50%	22.6	-5.09	6.77	11.50	2.24	-4.38
ESP 0% ESP 100%	8.23	-1.51	4.87	4.24	13.90	-4.44
COLE						
ESP 0% ESP 50%	0.018	-4.56	1.22	0.78	2.32	-1.02
ESP 0% ESP 100%	1.90	-4.21	3.77	-0.87	4.01	-0.700
Saturated Water Content						
ESP 0% ESP 50%	12.42	-1.93	8.14	6.30	20.3	9.11
ESP 0% ESP 100%	17.49	3.49	4.75	3.38	9.36	3.89
Water Content at -102 cm of H_2O						
ESP 0% ESP 50%	16.72	3.24	13.4	8.10	29.1	8.69
ESP 0% ESP 100%	12.71	0.29	4.67	5.44	21.90	1.29
-336 cm Water Content at -336 cm of H_2O						
ESP 0% ESP 50%	21.05	3.76	8.86	6.55	42.4	9.59
ESP 0% ESP 100%	15.18	0.92	3.46	5.31	43.7	1.92

Table 7 Functions to predict the soil liquid limit (LL) of natural soils based on multiple regressions, clay is in % CEC is in cmolekg^{-1}, $w_{1/3}$ is in g g^{-1}, COLE, ESP is in (%) and EC is in dS m^{-1}. The set labeled "1" is verification data using 25 % of samples from the prediction data set, and the labeled "2" is for soil survey characterization data from sodic soils where liquid limit was measured. COLE is not available in the soil survey data.

Function	RMSE (1) (%)	R^2 (1)	RMSE (2) (%)	R^2 (2)
LL=13.25+0.95*Clay	6.4	0.25	15.3	0.17
LL= 46.67+*0.067CEC	5.1	0.25	15.2	0.29
LL=23.9*55.3*$w_{1/3}$	3.9	0.71	12.8	0.26
LL=17.58+134.54*COLE	5.94	0.67		
LL=-7.78+0.92*Clay-0.49*EC+0.138*SAR+0.79*CEC	4.3	0.67	17.7	0.24
LL = 18.5-0.092*EC+0.062*ESP(%)+0.285*Clay(%)+0.601* CEC	4.63	0.66	12.21	0.32

Table 8. Functions to predict the plasticity index (PI) of soils using multiple linear regression. Clay is in (%), CEC is in cmole kg^{-1}, $w_{1/3}$ is in gg^{-1}, COLE, ESP is in (%), and EC is in dSm^{-1}. The data labeled "1" is the verification data using 25 % of samples from the prediction data set and data labled "2" is the soil survey characterization data from sodic soils where liquid limit we measured. COLE is not available in soil survey data.

Function	RMSE (1)	R^2 (1)	RMSE (2)	R^2 (2)
PI=5.19+0.539*Clay	4.3	0.16	8.7	0.10
PI=9.36+0.54*CEC	4.0	0.28	7.7	0.12
PI=10.25+31.86*$w_{1/3}$	3.5	0.70	7.25	0.25
PI=7.41+74.1*COLE	4.5	0.53		
PI=-9.87+0.49*Clay-0.018*EC+0.073*SAR+0.54*CEC	3.49	0.49	11.71	0.12
PI = 18.1-0.0031*EC+0.028*ESP(%)+0.117*Clay(%)+0.207*CEC	5.7	0.51	8.5	0.16

Table 9. Functions to predict the soil water content at -336 cm of H_2O($w_{1/3}$) matric potential . Clay is in %, CEC is in cmole kg^{-1}, $w_{1/3}$ is in g g^{-1}, COLE, ESP is in (%) and EC is in dS m^{-1}. Columns labeled “1” is for verification data using 25 % of samples from the prediction data set, and those labeled “2” are the soil survey characterization data from sodic soils where liquid limit was measured.

Function	RMSE (g g^{-1}) (1)	R^2 (1)	RMSE (g g^{-1}) (2)	R^2 (2)
$w_{1/3}$=0.19+0.0072*Clay	0.11	0.06	0.16	0.28
$w_{1/3}$=0.16+0.010*CEC	0.10	0.21	0.15	0.31
$w_{1/3}$=0.118+0.011*LL	0.062	0.71	0.17	0.26
$w_{1/3}$=0.066+0.015*PL	0.086	0.49	0.18	0.005
$w_{1/3}$=0.062+1.64*COLE	0.106	0.56		
$w_{1/3}$=-0.12+0.0063*Clay-0.012*EC+0.0032*SAR+0.011*CEC	0.061	0.72	0.21	0.012
$w_{1/3}$ =-0.076-0.013*EC+0.003*ESP(%)+0.0049*Clay(%)+0.00107*CEC	0.0406	0.88	0.189	0.024

Table 10. Functions to predict soil COLE using multiple linear regression equations. Clay is in %, CEC is in cmole kg^{-1}, $w_{1/3}$ is in g g^{-1}, COLE, ESP is in (%) and EC is in dSm^{-1}.

Equation	RMSE (mm mm^{-1})	R^2
COLE=0.142+0.0024*clay	0.051	0.07
COLE=0.125+0.0037*CEC	0.039	0.48
COLE=0.035+0.004*LL	0.030	0.67
COLE=0.11+0.005*PL	0.037	0.53
COLE=0.13 +0.22*$w_{1/3}$	0.036	0.55
COLE=0.035+-0.0013*EC+0.0076*SAR+0.0022*Clay+0.0038*CEC	0.036	0.55
COLE =0.045-0.013*EC+0.0074*ESP(%)+0.0017*Clay(%)+0.0038*CEC	0.033	0.60

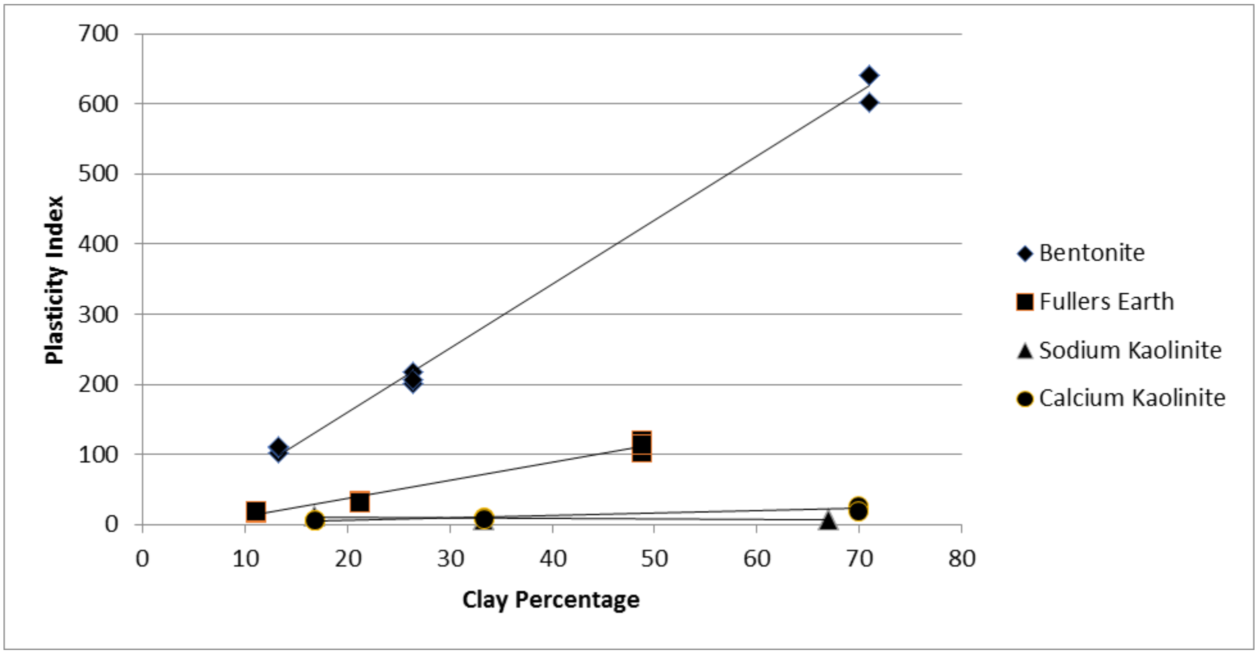

Figure 1. Effect of exchangeable cation on plasticity index for synthetic soils prepared from of clay mineral specimens and silt.

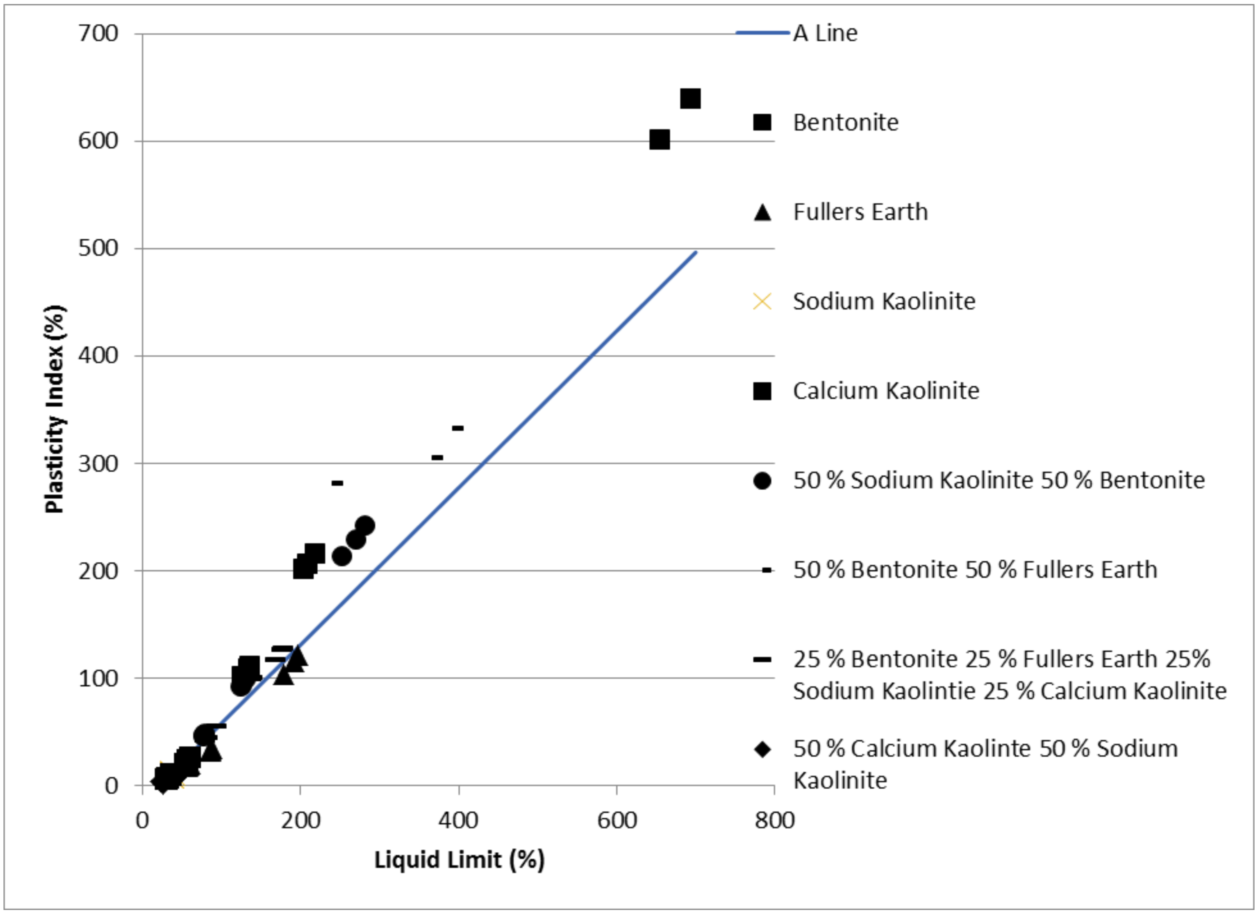

Figure 2. Casagrande plasticity chart for synthetic soils prepared from sodium and calcium saturated clay mineral specimens and silt.

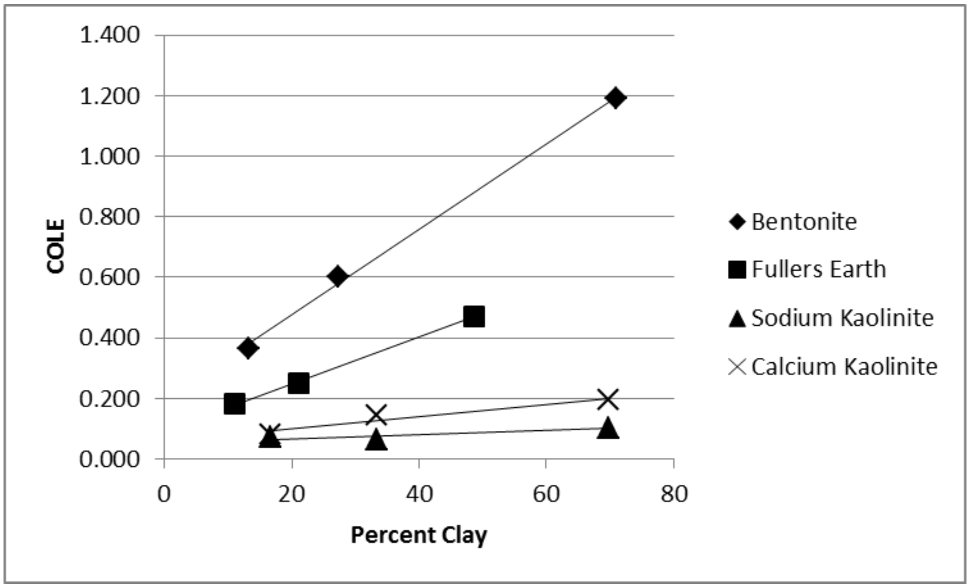

Figure 3. COLE vs percent clay for sodium smectite, calcium smectite, sodium kaolinite and calcium kaolinite, with percent clay as variable on the X axis, and COLE as the property on the Y axis.

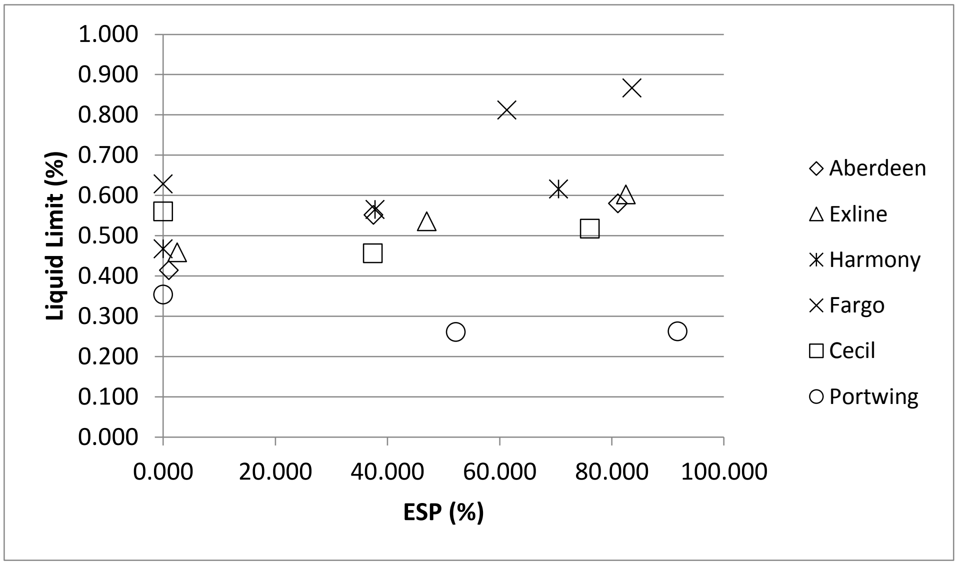

Figure 4. Liquid Limit vs ESP (%) for the Aberdeen, Cecil, Exline, Fargo, Harmony and Portwing soils at ESP treatments of 0%, 50% and 100%.

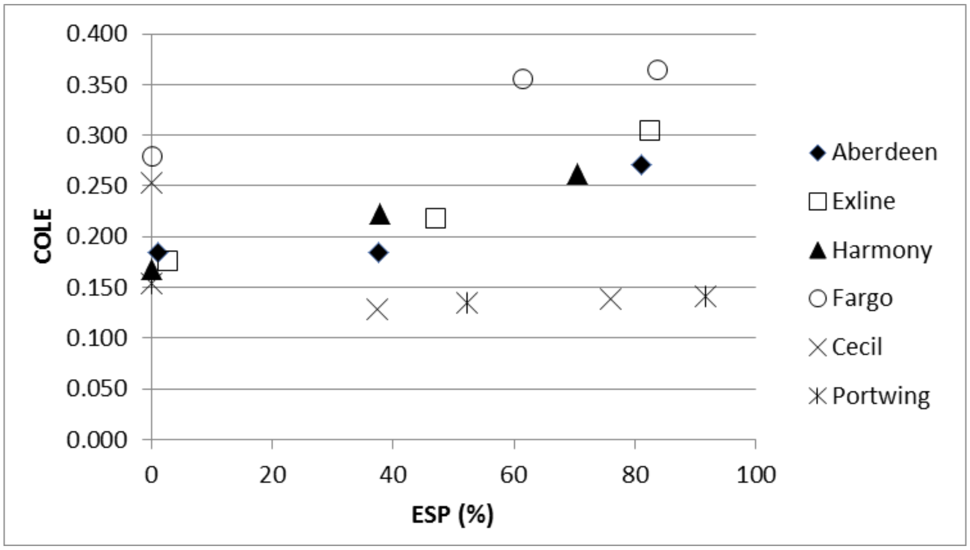

Figure 5. Soil coefficient of linear extensibility (COLE) vs exchangeable sodium percentage (ESP) for Aberdeen, Cecil, Exline, Fargo, Harmony and Portwing soils at ESP levels of 0%, 50% and 100%.

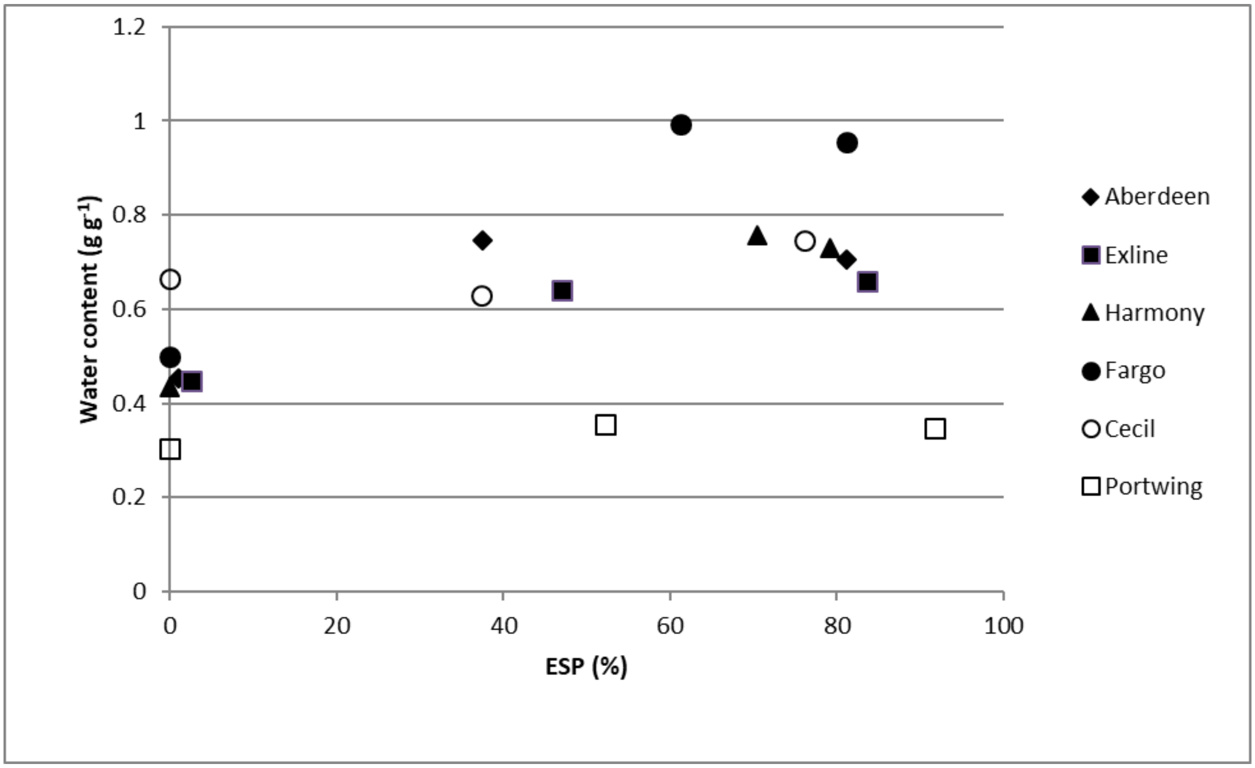

Figure 6 Soil water content at a matric potential of -102 cm of H_2O vs exchangeable sodium percentage (ESP) for the Aberdeen, Cecil, Exline, Fargo, Harmony and Portwing soils.

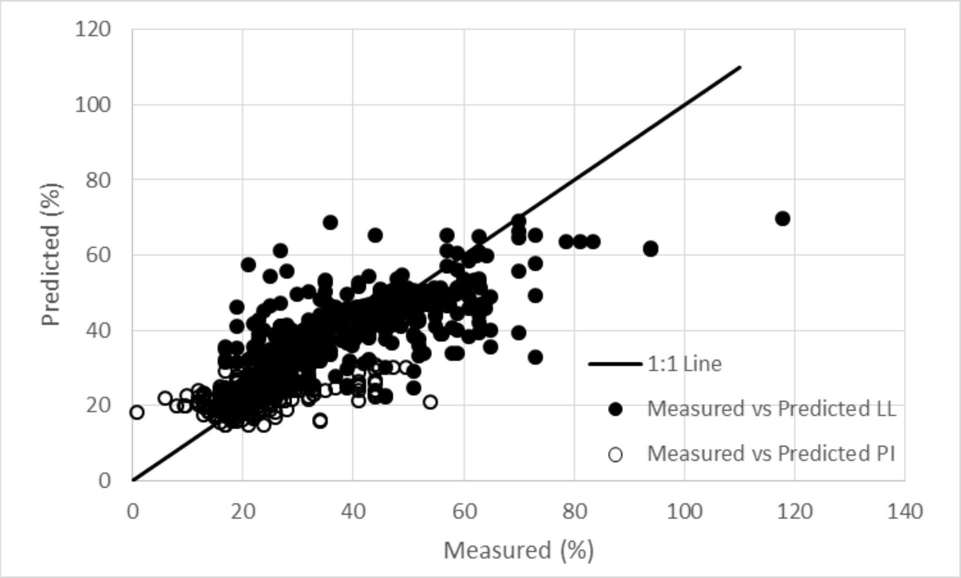

Figure 7. Measured vs predicted liquid limit and plasticity index for soils using the pedotransfer for liquid limit and plasticity index.

Chapter 3. Influence of Exchangeable Sodium and Clay Mineralogy on Soil Water Retention and Hydraulic Conductivity.

Abstract

Soil hydraulic properties are important for water management in salt and sodium affected soils. The hydraulic conductivity of saturated soil has been found to decrease when high soil solution sodium adsorption ratio (SAR) is coupled with low solution electrical conductivity (EC). Soil clay type has been found to play an important role in changes to soil hydraulic conductivity under solution composition of high SAR and low EC. The objective of this study was to determine the impact of a range of solution EC and exchangeable sodium percentage (ESP) values on the hydraulic conductivity of saturated soil and water retention for soils containing swelling and non-swelling clay minerals. The saturated hydraulic conductivity and water retention were measured on four smectitic soils, a kaolinitic soil and an illitic soil. Increasing soil solution ESP and decreasing EC level caused the saturated hydraulic conductivity to decrease and water retention to increase. Soil swelling causes large changes in soil hydrologic properties in smectitic soils due to high ESP and low EC levels whereas there is a reduced effect on non-smectite clay dominant soils.

Introduction

Soil sodicity and salinity are worldwide soil sustainability issues that are influenced by applied irrigation water and soil water management (Abrol et al., 1988). As the supply of freshwater resources in the world is decreasing the desire to use recycled and marginal water is increasing. Electrical conductivity is an index of the dissolved solutes in solution and SAR is a ratio which is calculated in equation (1) (Richards 1954), where sodium, calcium and magnesium levels are measured in mmol l^{-1} solution.

$$SAR = c_{Na}/\sqrt{c_{Mg} + c_{Ca}} \tag{1}$$

Soil salinity is high when crop growth or yields begin to decrease, commonly agreed to be 4 dS m^{-1}. It is unknown whether 4 dS m^{-1} salinity is a high enough threshold to prevent smectite clay swelling or flocculate clay or organic matter (Abrol 1998).

Soil salinity is known to increase the osmotic potential of soil water and reduce plant-available water, whereas soil sodicity is known to change soil structure (Richards 1954). Maintaining water flow through a soil and keeping the net water movement of the soil downward is important to prevent salinity build up in the plant root zone. The US Salinity Laboratory (USSL) considers soils with an exchangeable sodium percentage (ESP) ≥ 15 % or greater and a salinity level ≤ 4 dS m^{-1} to be sodic, soils with ESP ≥15% with a salinity ≥ 4 dS m^{-1} are classified as saline-sodic and soils with a salinity ≥ 4 dS m^{-1} and ESP ≤ 15 % are classified as saline (Richards, 1954). These ESP and salinity criteria along with the development of prismatic or columnar structure and the presence of an argillic subsurface diagnostic horizon is also required for the USDA Soil Taxonomy to classify soils as members of the various natric great groups (Soil Survey Staff, 2014).

Soil hydraulic conductivity is an important property related to soil water management and was the initial property measured to determine the impact of sodicity on soil physical properties (Quirk and Schofield, 1955). The soil hydraulic conductivity was found to decrease 10 % in a loam textured soil of mixed clay mineralogy at a salt concentration of 5 meq l^{-1} and 10 % ESP; the decrease continued as ESP reached 20 % requiring a salt concentration of 10 meq l^{-1}. This decrease in hydraulic conductivity relative to non-sodic condition (i.e. relative hydraulic conductivity) has been suggested as a threshold criterion. Quirk and Schofield (1955) considered a 10 to15% decrease in relative hydraulic conductivity as the threshold for a drastic reduction in relative hydraulic conductivity (Quirk and Schofield, 1955). These authors attributed the decrease in hydraulic conductivity to clay mineral swelling that caused pore blockage and clay deflocculating in response to high levels of sodium in solution relative to calcium and magnesium ions at low salt concentrations.

Relative saturated hydraulic conductivity measured on a variety of soils from the Southwestern United States revealed that some soils were more sensitive to the electrolyte composition and concentration of infiltrating waters than others (Frenkel et al., 1978 and McNeal et al., 1966). Soils that had a greater amount of clay and with a greater smectite content in the clay fraction required the highest electrolyte concentration to prevent a 25 % or greater decrease in relative saturated hydraulic conductivity from the high salinity state (McNeal et al.,1968 and McNeal and Coleman, 1966).

In a selection of soils with differing clay contents increasing the amount of smectite clay increased the sensitivity of the soil to infiltrating solution EC and SAR (McNeal et al., 1968). The relative saturated hydraulic conductivity of soils classified as Oxisols did not change until the iron oxides were chemically removed from the soil (McNeal et al., 1968).

McNeal (1968) developed a model to predict the effect of smectite clay mineralogy on relative saturated hydraulic conductivity. Others (Chiang et al., 1987 and Suarez et al., 1984) found that increasing solution pH caused increases in clay dispersion and decreases in relative saturated hydraulic conductivity. Increasing the pH of solution favors the exchange of sodium for calcium through compulsive exchange driven by calcite precipitation.

In a study combining soils of a range of texture and mineralogy in Australia, Bennett et al., (2019) found that the threshold curve (defined as a 20% relative decrease in saturated hydraulic conductivity with increasing ESP) correlated with the cation exchange capacity of the soils. Changes in saturated hydraulic conductivity have been related to clay swelling and aggregate breakdown caused by high ESP (Suarez et al., 1984 and Frenkel et al., 1978).

Soil water retention is an important property that affects plant-available water and water transport. The soil water retention is usually related to particle size distribution, organic matter content and bulk density of a soil (Gupta and Larson, 1979). The hydraulic conductivity of unsaturated soil can be predicted using the saturated hydraulic conductivity and the soil water retention curve (Mualem, 1976). Changes in soil pore structure and, therefore, hydraulic conductivity can be caused by soil salinity and sodicity.

Increasing salinity levels decreases the osmotic potential hence the total potential of soil water. Osmotic potential of the soil solution changes how water is stored and moves through soil (Zur, 1966). Clay mineralogy influences water retention because smectite clays retain greater amounts of water than illite and kaolinite clays (Macek et al., 2013). Furthermore, increasing soil osmotic potential prevents water from entering the interlayer of swelling smectite clay minerals, decreasing water retention at a given matric potential (Thyagaraj and Rao, 2010).

In smectitic soils from Sudan soil water retention increased at potentials greater than -15,000 cm of H_2O in clay textured vertisols as solution EC decreased and sodium adsorption ratio increased (Malik et al., 1992). Water retention was found to increase at water potentials of -336cm of H_2O in smectitic and mixed clay mineralogy soils from North Dakota and Saskatchewan (He et al., 2013 and Curtain et al., 1994). Soil water retention gradually increased at ESP levels between 2 and 15 in a mixed clay type soil at a salt concentration of 3 meq l^{-1} (Crescimano et al., 1995). These changes in water retention were due to a combination of swelling of smectite in clay fraction and break down of soil aggregates from high sodium levels and low salt concentrations (Malik et al., 1992).

There were four objectives of this study. The first objective was to determine changes in soil hydrologic properties from increasing ESP and varying salt concentrations for soils of different clay types. The second objective was to determine the change of soil relative saturated hydraulic conductivity related to smectite clay swelling. The third objective: determine changes in soil water retention due to soil clay types for a range of solution EC and soil ESP values. Fourth, determine changes in the soil water retention shape fitting parameters due to differences in solution EC and soil ESP.

Methods

Soil Collection

Three smectitic silty clay loam soils were collected from South Dakota (Aberdeen, Exline and Harmony) from argillic or natric horizon. Harmony series (Fine, smectitic, frigid Pachic Argiudolls) was collected at 44.9827 N, 98.5088 W from 30-50 cm depth, Aberdeen soil series (Fine, smectitic, frigid Glossic Natrudolls) was collected at 44.9553 N, 98.4426 W from 25-45 cm depth and the Exline soil series (Fine smectitic frigid Leptic Natrudolls) was collected at 44.9550 N, 98.4229 W from 15 to 40 cm depth Argillic horizon from Portwing soil (Fine, mixed, active ,frigid Oxaquic Glossudalf) from Wisconsin and the argillic horizon at 46.837N, 91.08W of a clay textured kaolinitic Cecil (fine kaolinitic, thermic Typic Kanhapludult) Soil from North Carolina at 35.7335 N, 78.6717 W. Fargo soil (Fine, smectitic, frigid Typic Epiaquert) from the A horizon of a silty clay veritsol was collected from North Dakota at 47.1729 N,96.9003 W.

Soil Characterization

Particle size distribution of the soils was measured using the pipette method (Deshpande and Telang, 1950). Exchangeable cations were measured using a 1M CsCl extract. Soluble cations and salinity of the soils were determined using a 1:1 soil to water extract. Cations present in saturated paste extract, 1:1 soil to water extract and CsCl extract were measured using ICP-OES Perkin Elmer Optima 4300 DV.

X-ray diffraction was measured on soil clay fractions isolated by dispersing soil with 50 g l^{-1} sodium hexametaphosphate and removing the top 10 cm of liquid after all particles larger than 2 um were settled out of top 10 cm. After samples were dried and crushed X-ray diffraction was then measured on a homogenized < 2um fraction. The clay fraction mineralogy of the Aberdeen, Exline, Fargo and Harmony soils was mostly smectite and illite with small amounts of kaolinite and quartz in the samples. The Portwing soil clay fraction mineralogy was primarily illite with small amounts of smectite, kaolinite, hematite and quartz, whereas the Cecil soil clay fraction mineralogy was primarily kaolinite with small amounts of hematite, gibbsite and quartz within the soil.

Soil Column Treatments

The soils were placed into 7.5 cm diameter PVC columns and packed to a uniform bulk density and the soil columns treated with 1 molar $NaCl$-$CaCl_2$ solutions to create ESP levels between 0% and 50% (ESP treatment levels of 0, 6, 15, 25 and 50) for approximately 5 pore volumes followed by a sequential drop to electrolyte concentrations of 40 meq l^{-1}, then 20 meq l^{-1} followed by 10 meq l^{-1} and finally 5 meq $;^{-1}$ using the measured (Na^+, Ca^{2+}) exchange selectivity of $K_{Na/Ca}$=0.22 using the Vanselow convention (Vanselow 1932). After the outflow EC was equal to inflow EC the soil was air dried and crushed to pass through a 2mm sieve.

Dry Treatment for Water Retention

For the low salinity treatments 10 meq l^{-1} (ESP 50 %) and 5 meq l^{-1} (ESP 6, 15, 25 and 50%) the soils were treated with dry sodium carbonate based on ESP percentage, taking into account pore water composition. Dry sodium carbonate was added to the 5 meq l^{-1} ESP 0% treatments or 10 meq $;^{-1}$ ESP 0% treatment as needed.

Sodium carbonate equal to one half of the CEC was added to the soil to create the ESP 50 % treatment, while sodium carbonate equal to the CEC was added to the soil to create the 100 % ESP treatment. For example, the amount of sodium carbonate added to the Harmony soil was 12.1 $cmol_cNa^+$ kg^{-1} soil or 6.41g Na_2CO_3 kg^{-1} soil for ESP 50% and ESP 100%, respectively. The ESP levels of the sodium carbonate treatments and EC 1:1 extract value is listed in Table 3 After the sodium carbonate was mixed with the dry soil the soil was packed to a bulk density of 1.15 g cm^{-3}.

Water Retention Curve

The treated soils were capillary wetted with deionized water for a week then weighed; this was the saturated water content. The soil samples were then placed on a tension table and equilibrated to pressure heads of -10 cm of H_2O, followed by -25 cm, -50 cm, -100 cm, -200cm and -300 cm of H_2O matric potential on the same samples. A second stage of measurements required transfer of samples to a pressure chamber where they were equilibrated in sequence to pressure heads equivalents of -336 cm, -1020 cm, -2040 cm and -4080 cm of H_2O matric potential. After the -4080 cm matric potential was measured on the soil samples, the soil samples were air dried at 105 degree C for 48 hours before determining the oven dry soil mass.

Four grams of equilibrated soil from each treatment was placed into metal containers to measure water retention on WP4C Dewpoint Potentiometer (Meter Group, Pullman WA) This instrument measures the relative humidity of the air in a closed chamber near the surface of a soil and correlates it to the total water potential. There was no difference in the high salinity treatments compared to the low salinity treatments so there was no correction for osmotic potential. The samples were saturated and allowed to dry to water potentials of approximately -10000 cm of H_2O total potential, then covered and allowed to equilibrate at the given moisture content for 24 hours. The samples were then measured on the WP4C and weighed after the total potential measurement to determine the water content. The soil was allowed to dry for an hour, then covered and allowed to equilibrate overnight. Measurements with the WP4C were made again as described above. This process was repeated until the soil samples reached -100,000 cm of H_2O total potential. The gravimetric water content of these samples was then determined after the samples were air dried for 48 hours. This procedure was done at salinity treatments ranging from 5 and 40 meq l^{-1} and ESP levels between 0 and 50% on the Aberdeen, Exline and Harmony soils along with ESP of 0, 50 and 100% dry treatments on all soils

Hydraulic Conductivity

Hydraulic conductivity was measured on the Aberdeen, Exline, Harmony, Fargo, Portwing and Cecil soils. The soils were packed to a uniform bulk density for each soil type using the same packing procedure described above. The Aberdeen, Exline and Harmony soils were packed to a bulk density of 1.15 g cm^{-3}, the Fargo soil was packed to a bulk density of 1.05 g cm^{-3} and the Cecil and Portwing soils were packed to a bulk density of 1.25 g $cm\text{-}^{3}$ due to soil arranging to different bulk densities when using a uniform soil packing procedure.

Hydraulic conductivity was measured at ESP percentages of 0, 6, 15 and 25% at salt concentrations of 5, 10, 20 and 40 meq l^{-1}. The soil was wetted with the 40 meq l^{-1} treatment at a given SAR level until it was saturated. The soil was then infiltrated with a solution at a given

SAR value until the saturated hydraulic conductivity reached a steady state. After hydraulic conductivity reached a steady state, the infiltrating solution was dropped to the next lower salt concentration to create the same ESP value. Once the hydraulic conductivity value reached a steady state at the next lowest salt concentration of 20 meq l^{-1} the procedure was repeated for the 10 meq l^{-1} and 5 meq l^{-1} treatments. Soil was air dried and homogenized after the 5 meq l^{-1} treatment to determine ESP of the treatment listed in (Appendix Table 1). The relative hydraulic conductivity was calculated using a linear regression of EC vs Ksat at a given ESP % and solving for the saturated hydraulic conductivity of the 40 meq l^{-1} ESP 0 treatment multiplied by 0.75 for a given soil. A threshold value of 25% for relative hydraulic conductivity was used similar to that used by McNeal et al., (1968).

Water Retention Curve Fitting

Water retention curves were fit with the van Genuchten (1980) constrained model (2) where w_s is the saturated water content in (g g^{-1}), w_r is residual water content (g g^{-1}), α is the inverse of the air entry point (-cm) and n is a pore size distribution parameter.

$$w_r \frac{w - w_r}{w_s - w_r} = S_e = \frac{1}{[1 + (\alpha|h|^n)]^m} \tag{2}$$

$$m = 1 - \frac{1}{n} \tag{3}$$

Statistical Analysis

An ANOVA was used is SAS 9.4 to determine changes in saturated hydraulic conductivity or the fitting parameters for van Genuchten fitting parameters. The saturated hydraulic conductivity, w_s, α, n were each compared for soil effect, soil by EC, soil by ESP and soil EC by ESP effects. Due to each soil being statistically significant from each other the saturated hydraulic conductivity, w_s, α, n parameters were analyzed for significance of EC, ESP and EC by ESP effects on each individual soil. The values were analyzed using a mixed effect ANOVA with significance at alpha =0.05

Results

The hydraulic conductivity of saturated soil was highest in the kaolinitic Cecil soil and the illitic Portwing soil and was much lower in smectitic soils regardless of solution EC and SAR (Figure 1). The relative hydraulic conductivity of saturated soil was lowest for the 5 meq l^{-1} ESP 15% and ESP 25% treatments for all the soils (Figure 1). The relative saturated hydraulic conductivity required a higher salt concentration to maintain the same flow rate at the 40 meq l^{-1} ESP 0% treatment in the smectitic soils when compared to the non smectitic soils (Figure 1).

The relative hydraulic conductivity of 25% occurred at a higher salt concentration at a given ESP percentage in the smectitic soils compared to the non-smectitic soils. (Figure 2). The relative hydraulic conductivity threshold of illitic Portwing loam and kaolinitc Cecil clay soils were similar to the threshold on the Rothamstead loam (Quirk and Schoefield, 1955) and loamy mixed-clay soils from California (McNeal and Coleman, 1966) at low SAR levels. Increasing SAR above 15 caused the illitic loam and kaolinitc clay to be more sensitive than the Quirk and Schofield threshold.

The smectitic soils in our study behaved like the highly sensitive Gila soil from McNeal and Coleman (1966) and the most sensitive soils relative hydraulic conductivity threshold curve from Bennett et al., (2019) on Austrailian soils. The smectitic soils have a smaller range of useable EC and SAR combinations of infiltrating solutions compared to the non smectitic soils where soil hydrologic properties do not change.

Soil water retention was initially measured on the Aberdeen, Exline and Harmony soils at EC levels of 5, 10, 20 and 40 meq l^{-1} and ESP percentages of 0, 6, 15, 25 and 50%. The water retention in these soils gradually increased as ESP increased from levels of 0 to 15% at the 5 meq l^{-1} ESP level (Figures 3, 4 and 5). Soil ESP increases from 15 to 25% and, again, from 25 to 50 % resulted in large increases in soil water retention in the range from saturation to -15,300 cm H_2O matric potential (Figures 3, 4 and 5).

Maintaining high salinity levels (40 meq l^{-1}) suppressed increases in water retention related to ESP-induced smectite clay swelling. Although soil water retention increased at ESP 50 % for all salinity levels, increasing the solution EC to 40 meq l^{-1} cancelled the effect of high ESP on soil water retention.

Soil water retention was measured also measured at ESP percentages of 0, 50 and 100 % prepared using a dry sodium carbonate treatment on the Aberdeen, Fargo, Portwing and Cecil soils. The soils that were smectitic (Aberdeen and Fargo) showed large increases water retention by swelling clays as increases from ESP 0% to ESP 50% and ESP 100% (Figure 6). The illitic soil which had less smectite in clay fraction had a smaller increase in its soil water retention, whereas the kaolinitic soil had no increase in its soil water retention from increasing ESP values (Figure 6).

The α and n parameters did not follow a consistent trend based upon solution EC and ESP level with the α parameter having a large range of values whereas the n parameter values fell within a smaller range (Table 2). Changing value of the saturated water content can cause the shape fitting parameters to shift if the water retention is the same at a potential such as –50 cm H_2O of matric potential. If the water content is 0.5 g g^{-1} at -50 cm of H_2O and the w_s is 0.7 g g^{-1} for one treatment and 0.65g g^{-1} for another treatment, the treatment with the w_s=0.7 g g^{-1} will have a smaller n parameter and larger α parameter. The w_s value increased at low EC and high

ESP treatments with increasing salinity masking the effects of high ESP levels (Table 2). The saturated hydraulic conductivity decreased as ESP increased at low salinity levels.

On soil prepared using dry treatments the fitting parameters did not change on the kaolinitic soil. In contrast, the w_s values increased on the illitic soil and all the smectitic soils (Table 3). The α parameter decreased and the n parameter increased on some of the smectitic soils (Table 3). Increasing soil ESP level clearly increased saturated water content on soils that contained appreciable smectite.

Discussion

The hydraulic conductivity of saturated soil was higher for the non smectitic soils than for the smectitic soils with the lowest relative hydraulic conductivity values at a given treatment level recorded on the smectitic Fargo soil. All soils showed decreased relative saturated hydraulic conductivity at the lowest salinity value and highest ESP treatment although how it changed with EC by ESP combination differed between soils. The smectitic soils required a greater salt concentration relative to the non-smectitic soils to maintain the same flow rate even at low ESP treatments. The smectitic soils also had a lower initial saturated hydraulic conductivity and had flow rates drop to lower levels at high EC and low ESP treatments

The smectitic soils had a greater relative hydraulic conductivity decrease between the 40 meq l^{-1} ESP 0% treatment and the 5 meq l^{-1} ESP 25% treatment where absolute hydraulic conductivity were consistently less than 0.2 cm day^{-1}. Smectitic soils and soils with a higher CEC also have been found to have greater changes in saturated hydraulic conductivity in previous studies on soils of a variety of mineralogy types (Bennett et al., 2019 and McNeal et al., 1996).

When creating threshold curves for relative saturated hydraulic conductivity vs salt concentration (cf. Figure 2) each soil had its own threshold curve. The smectitic soils behaved similarly to the Gila soil and the most sensitive soil from Austrailia (Bennett et al., 2019), whereas the illitic and kaolinitic soils behaved like the Rothamsted soil and intermediate sensitivity soils from the McNeal study (Bennett et al., 2019, McNeal et al., 1966 and Quirk and Schofield, 1955).

The relative decrease in saturated hydraulic conductivity may not be that important to water and salinity management if the soil does not retain a lot of water under field conditions or if the soil net water balance is not changed from downward to upward from the soil hydrologic conditions. Downward net water movement will mean the solutes are being flushed downward in the soil whereas upward net water movement concentrates soil solutes near soil surface.

Soil water retention was similar for the three smectitic soils from South Dakota across the solution treatments that were applied to them. The ESP 50% treatment increased water retention at values between saturation and -15300 cm of H_2O matric potential at all salinity level between 5 and 40 meq l^{-1}. For the 5 meq l^{-1} ESP 0% treatment water retention increased gradually between ESP values of 0 and 15% and rapidly increased once the ESP value was increased to an ESP of 25%. Increasing the salinity value delayed the ESP level where water retention began to increase, which is in agreement with the behavior of smectite clay where the osmotic potential of soil water can prevent water from entering smectite clay interlayers (Norrish and Quirk, 1955).

Treating the smectitic soils with sodium carbonate increased interlayer water uptake by a large margin at water potentials from saturation to water potentials between -10000 and -20000 cm of H_2O matric potential of pressure head. At this negative of a matric potential (-20000 cm of H_2O matric potential) water can be drawn out of the interlayers of smectite clay minerals, therefore water retention should be dependent solely upon the specific surface area of the material (Macek et al., 2013).

As the soil becomes wetter and matric potentials decrease water begins to enter the interlayer of sodium-saturated smectite clay minerals. Smectite clay minerals that are sodium saturated can absorb more than two layers of water within the interlayers. The rest of the water is absorbed to the surfaces of particles. The kaolinitic soil revealed no increases in water retention from increasing the exchangeable sodium percentage. The illitic Portwing soil had a smaller increase in its water retention from the increase in exchangeable sodium percentage compared to the smectitic soils.

Increasing exchangeable sodium percentage at low EC does two things: it decreases the degree of flocculation of soil organic matter and clay particles and it increases the swelling of smectite clay minerals (Klopp et al., in review and Shainberg et al., 1981). For (EC, and ESP) treatments where there was a large change in physical properties responsive to clay swelling (e.g, Atterberg liquid limit and the whole-soil coefficient of linear extensibility) there was a large increase in soil water retention that extends to water potentials negative enough to draw water out of the interlayers of a sodium saturated smectite. This also correlated to a large drop in saturated hydraulic conductivity at high ESP and low EC levels.

The van Genuchthen parameters (Table 2) changed in response to (EC and ESP) treatments for the Aberdeen, Exline and Harmony soils. The w_s parameter increased at high ESP and low salinity values otherwise the fitting parameters had no consistent trend based upon the EC* ESP combination. High salt concentrations decrease overall swelling and saturated water content in disturbed soil samples that did not have their soil volume confined while wetting. In a state where bulk swelling would be reduced there would be an increase in the air entry value. (α^{-1}) and an increase in the n value.

When comparing the ESP 0% to the ESP 50% and ESP 100% treatments there was a large increase in the w_s value for the smectitic soils. For the non smectitic soils there were no changes in the soil water retention curve fitting parameters in the kaolinitic soils, while there was an increase in the w_s value in the illitic soil. The w_s increased from swelling of the smectite clay in the soil. Increasing ESP while maintaining low EC increases the amount of water retained but only caused small changes to the shape of the curve. There is a small decrease in α which is the inverse of the air entry point and an increase in the n value. Confining the volume of the soil sample may lead to different changes in the shape fitting parameter of the water retention curve under conditions that create a high degree of swelling.

The hydraulic conductivity of saturated soil changed for all soils but had greater decreases in the smectitic soils. Water retention increased by 90% on the smectitic soils 32% on the illitic soil and by 4 % on the kaolinitic soil at a potential of -336 cm of H_2O. Clay mineral swelling plays a large role in changes of saturated hydrologic properties on smectitic soils whereas soils that contain little smectite within the clay fraction have no change is soil swelling. In the smectitic soils a combination of clay swelling and aggregate breakdown causes soil hydrologic properties to change whereas in soils with low amounts of smectite clay only the breakdown of aggregates can also cause changes in soil hydrologic properties.

Conclusions

Soil saturated hydraulic conductivity decreased as ESP level increased and salinity level decreased on soils consisting of three different types of dominant clay mineralogy. The smectitic soils had a much greater change in saturated hydraulic conductivity and changed at lower ESP levels compared to the non-smectitic soils. Soil water retention increased as EC of the solution decreased, and ESP of the solution increased. Soils that contained high amounts of smectite had a large increase in water retention at high ESP values compared to the illitic and kaolinitic soils. Water retention gradually increased at low ESP levels and more rapidly increased at ESP levels of 25% or greater at low salt concentrations. The water content at saturation increased as ESP increased in the smectitic soil and the illitic Portwing soil although none of the other water retention curve fitting parameters changed by salt concentration and ESP combinations.

Smectitic soils had larger changes in the soil hydrologic properties compared to the illitic and kaolinitic soils because there were large increases in water retention due to swelling of the smectite clays. Smectitic soils have a large increase in water retention at high ESP and low EC levels due to free swelling which will block large pores, reducing hydraulic conductivity and increasing soil water retention in or near saturated soil conditions.

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Tables and Figures

Table 1. Sand , silt and clay contents, cation exchange capacity (CEC) exchangeable sodium percentage (ESP), electrical conductivity (EC) and USDA soil texture classification for the soils used in this study.

Soil	Sand (%)	Silt (%)	Clay (%)	CEC cmole$_c$ kg^{-1}	ESP (%)	EC (dS m^{-1})	USDA Classification
Cecil	24.3	25.7	50.0	4.56	1.7	0.624	Clay
Fargo	1.6	48.5	49.9	24.5	0.001	0.489	Silty Clay
Aberdeen	1.90	61.2	36.9	21.1	11.4	0.660	Silty Clay Loam
Exline	3.10	61.4	35.5	18.7	37.0	3.15	Silty Clay Loam
Harmony	10.1	59.0	30.9	25.4	0.967	0.590	Silty Clay Loam
Portwing	30.9	44.4	24.7	7.60	0.00	0.370	Loam

Table 2. Van Genuchthen fitting parameters for Aberdeen, Exline and Harmony soils treated with different electrical conductivity (EC) and exchangeable sodium percentages (ESP) combinations. The water content at saturation (w_S), residual soil water content (w_r), the α is the inverse of air entry point, n is pore size parameter, and hydraulic conductivity of saturated soil (Ks) are reported here. Mean values within individual soils with different letters are statistically different from each other at a 0.05 level.

Soil	EC meq l^{-1}	ESP (%)	w_S (g g^{-1})	w_r (g g^{-1})	α (-cm)	n	Ks (cm day^{-1})
Aberdeen	5	0	0.619e	0	0.094bc	1.15d	2.76c
Aberdeen	5	6	0.756b	0	0.40a	1.16cd	4.53bc
Aberdeen	5	15	0.667de	0	0.035c	1.20b	0.078c
Aberdeen	5	25	0.770b	0	0.098bc	1.19b	0.092c
Aberdeen	5	50	0.982a	0	0.020c	1.24a	
Aberdeen	40	0	0.65de	0	0.11bc	1.16cd	12.4a
Aberdeen	40	6	0.686cd	0	0.385a	1.16cd	10.5ab
Aberdeen	40	15	0.693cd	0	0.133bc	1.19b	2.72c
Aberdeen	40	25	0.738bc	0	0.235ab	1.16cd	5.14bc
Aberdeen	40	50	0.657de	0	0.0278c	1.18bc	
Exline	5	0	0.713cd	0	0.268ab	1.15d	7.34ab
Exline	5	6	0.746c	0	0.348a	1.16cd	4.84ab
Exline	5	15	0.650de	0	0.018b	1.22a	0.029b
Exline	5	25	0.859b	0	0.160ab	1.18b	0.072b
Exline	5	50	0.998a	0	0.116ab	1.12e	
Exline	40	0	0.647e	0	0.079b	1.18bc	10.04a
Exline	40	6	0.667de	0	0.235ab	1.17d	3.2ab
Exline	40	15	0.687cde	0	0.194ab	1.18bc	9.71a
Exline	40	25	0.803b	0	0.214ab	1.18b	1.75ab
Exline	40	50	0.657de	0	0.027b	1.18bc	
Harmony	5	0	0.661c	0	0.179ab	1.16c	4.19cd
Harmony	5	6	0.564d	0	0.016b	1.21ab	1.49d
Harmony	5	15	0.699c	0	0.031ab	1.20ab	0.081d
Harmony	5	25	0.937a	0	0.180ab	1.18bc	0.021d
Harmony	5	50	0.971a	0	0.027ab	1.21ab	
Harmony	40	0	0.670bc	0	0.039ab	1.21ab	9.71b
Harmony	40	6	0.732b	0	0.17ab	1.18bc	8.39bc
Harmony	40	15	0.776b	0	0.319a	1.16bc	7.15bc
Harmony	40	25	0.786b	0	0.271ab	1.18bc	17.0a
Harmony	40	50	0.664c	0	0.019ab	1.22a	

Means were compared with individual soils. Samples with different letters are statistically significant

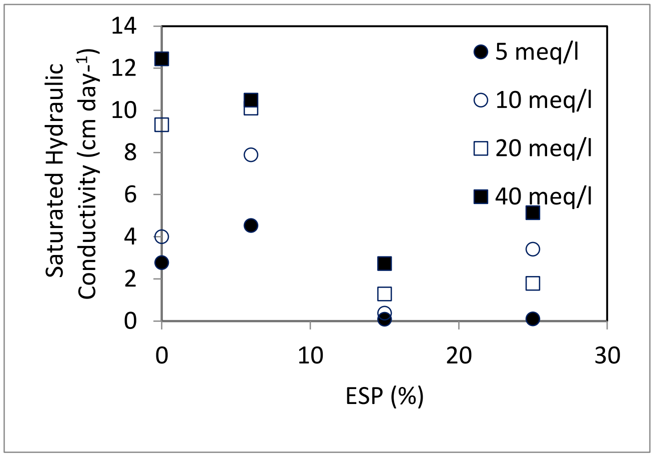
Table 3. Van Genuchthen fitting parameters for dry treatments at 5 meq L^{-1} at exchangeable sodium percentages (ESP) of 0%, 50%, and 100 %. The soil water content at saturation (w_s), residual water content (w_r), the α is the inverse of air entry point, *n* is pore size parameter, and the hydraulic conductivity of saturated soil (Ks) are reported here. Mean values within individual soils with different letters are statistically different from each other at a 0.05 level.

Soil	ESP (%)	EC 1:1 dSm^{-1}	ESP meas (%)	w_s ($g\ g^{-1}$)	w_r ($g\ g^{-1}$)	α (-cm)	N
Cecil	0	0.576	0	0.66b	0	0.174a	1.17a
Cecil	50	0.909	62.3	0.63b	0	0.143a	1.15a
Cecil	100	1.64	76.1	0.74a	0	0.477a	1.16a
Fargo	0	0.500	0	0.76b	0	0.359a	1.14b
Fargo	50	1.00	61.3	1.27a	0	0.0186a	1.23a
Fargo	100	1.59	83.6	1.31a	0	0.0385a	1.22a
Aberdeen	0	0.337	1.00	0.62b	0	0.0937a	1.15b
Aberdeen	50	0.585	37.4	0.98a	0	0.0200b	1.24a
Aberdeen	100	0.971	81.1	1.03a	0	0.0522b	1.20a
Exline	0	0.471	2.50	0.71b	0	0.269a	1.15b
Exline	50	0.602	47.0	1.00a	0	0.116b	1.20a
Exline	100	0.701	82.5	0.97a	0	0.0789b	1.20a
Harmony	0	0.580	00	0.66b	0	0.179b	1.16b
Harmony	50	0.861	37.8	0.97a	0	0.0274b	1.21ab
Harmony	100	1.22	70.5	1.02a	0	0.0135b	1.26a
Portwing	0	0.186	0.00	0.44b	0	0.140b	1.17a
Portwing	50	0.805	52.2	0.52b	0	0.0659c	1.19a
Portwing	100	1.26	91.7	0.62a	0	0.360a	1.18a

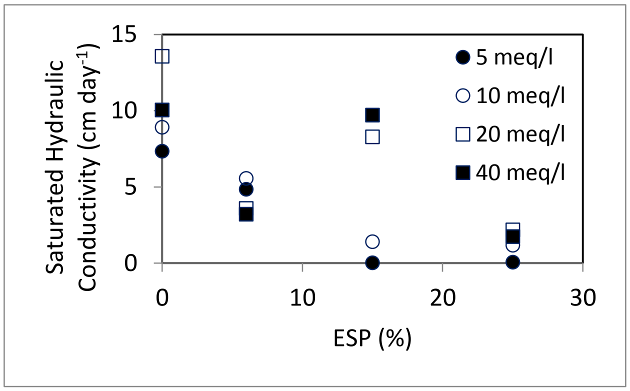
Appendix Table 1 Soil, Treatment solution and 1:1 Extract EC and ESP value created by treatments of solutions to create a given ESP level

Soil	Treatment (%)	EC solution (ds m^{-1})	EC 1:1 (dS m^{-1})	ESP (%)
Aberdeen	ESP 0	0.489	0.244	3.6
Aberdeen	ESP 6	0.507	0.374	6.20
Aberdeen	ESP 15	0.934	0.741	11.3
Aberdeen	ESP 25	0.861	0.590	22.8
Cecil	ESP 0	0.648	0.321	0
Cecil	ESP 6	0.642	0.164	13.0
Cecil	ESP 15	0.515	0.308	13.0
Cecil	ESP 25	.553	.553	25.8
Fargo	ESP 0	0.474	0.45	0
Fargo	ESP 6	0.950	0.647	5.30
Fargo	ESP 15	1.10	0.589	11.5
Fargo	ESP 25	1.22	0.67	11.1
Exline	ESP 0	0.468	0.468	2.6
Exline	ESP 6	0.510	0.360	12.1
Exline	ESP 15	0.651	0.433	21.8
Exline	ESP 25	0.661	0.336	25.7
Harmony	ESP 0	0.436	0.556	0.001
Harmony	ESP 6	0.436	0.433	8.77
Harmony	ESP 15	0.728	0.363	10.7
Harmony	ESP 25	1.31	0.42	17.5
Portwing	ESP 0	0.6	0.207	2.5
Portwing	ESP 6	0.537	0.537	4.98
Portwing	ESP 15	0.429	6.31	15.6
Portwing	ESP 25	0.664	0.247	19.5

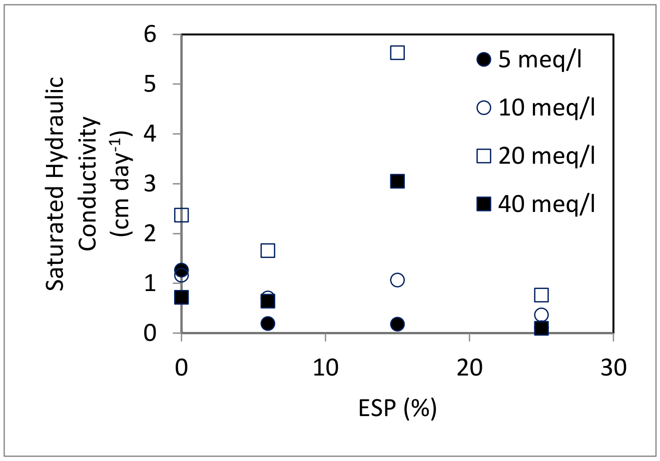
Figure 1. Relationship between hydraulic conductivity of saturated soil and exchangeable sodium percentage (ESP) for 5, 10, 20, and 40 meq L^{-1} treatments. The soil used are smectitic soil; Aberdeen (a), Exline (b), Fargo (c) and Harmony (d); and ilitic soil Portwing (e) and Cecil (f) at ESP values between 0 and 25%.



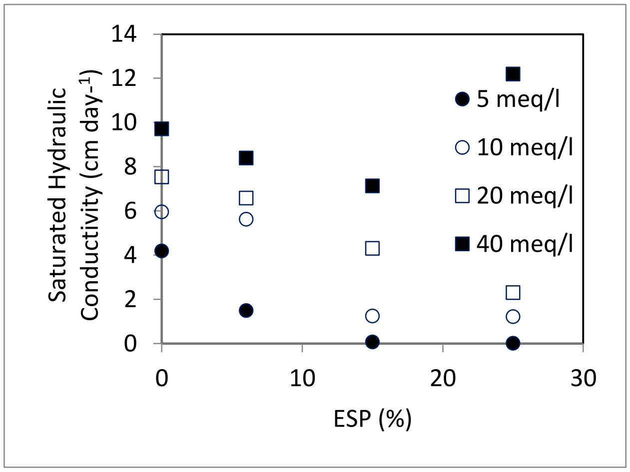
(a)



(b)

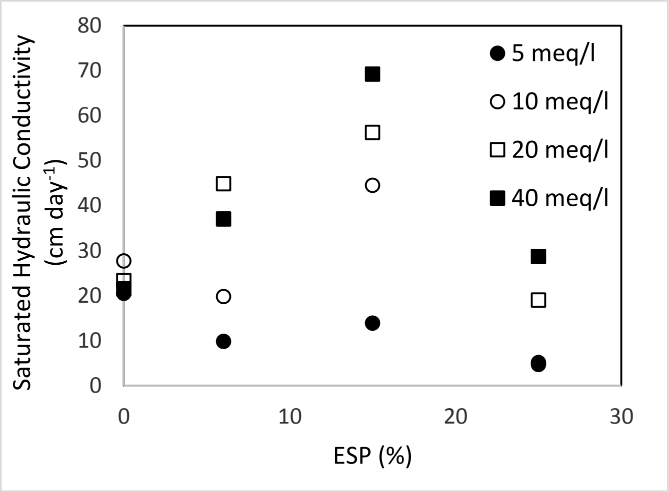

Saturated Hydraulic Conductivity (cm day^{-1})
ESP (%)
0
1
2
3
4
5
6
0
10
20
30
● 5 meq/l
○ 10 meq/l
□ 20 meq/l
■ 40 meq/l

(c)


Saturated Hydraulic Conductivity (cm day^{-1})
ESP (%)
0
2
4
6
8
10
12
14
0
10
20
30
● 5 meq/l
○ 10 meq/l
□ 20 meq/l
■ 40 meq/l

(d)

(e)


Saturated Hydraulic Conductivity (cm day^{-1})
80
70
60
50
40
30
20
10
0
0
10
20
30
ESP (%)
● 5 meq/l
○ 10 meq/l
□ 20 meq/l
■ 40 meq/l

(f)

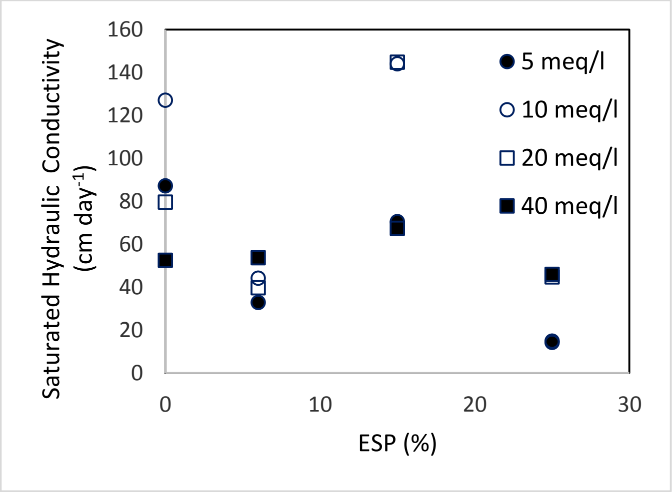
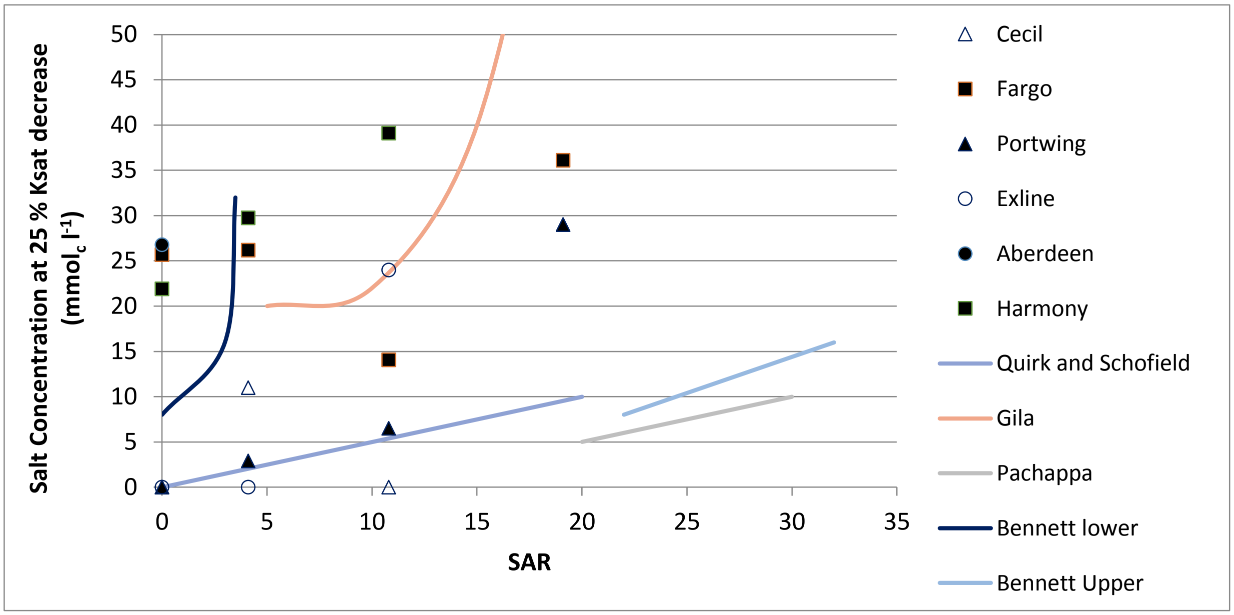
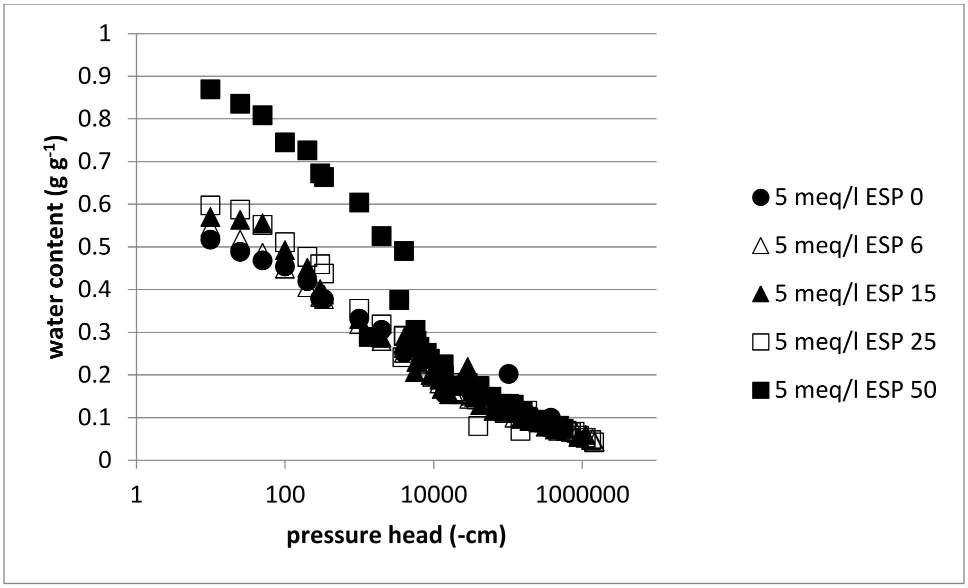

Saturated Hydraulic Conductivity (cm day^{-1})
160
140
120
100
80
60
40
20
0
0
10
20
30
ESP (%)
● 5 meq/l
○ 10 meq/l
□ 20 meq/l
■ 40 meq/l

Figure 2. Hydraulic conductivity at a 25 % relative decrease from the hydraulic conductivity of saturated untreated soil of the 40 meq l^{-1} ESP 0% treatment.





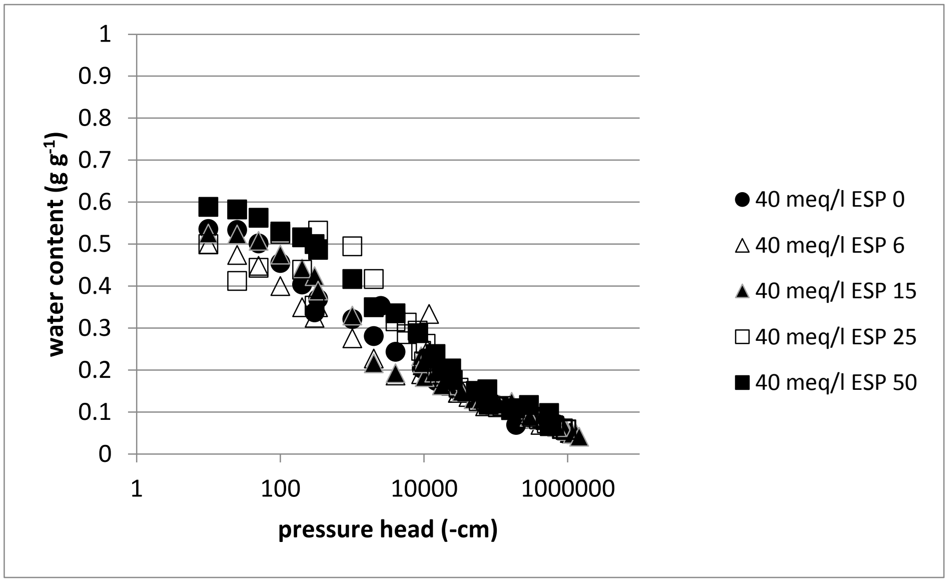


Figure 3. Water retention curves for the Aberdeen soil at salt concentrations of 5 and 40 meq l^{-1} at different exchangeable sodium percentages (ESP)

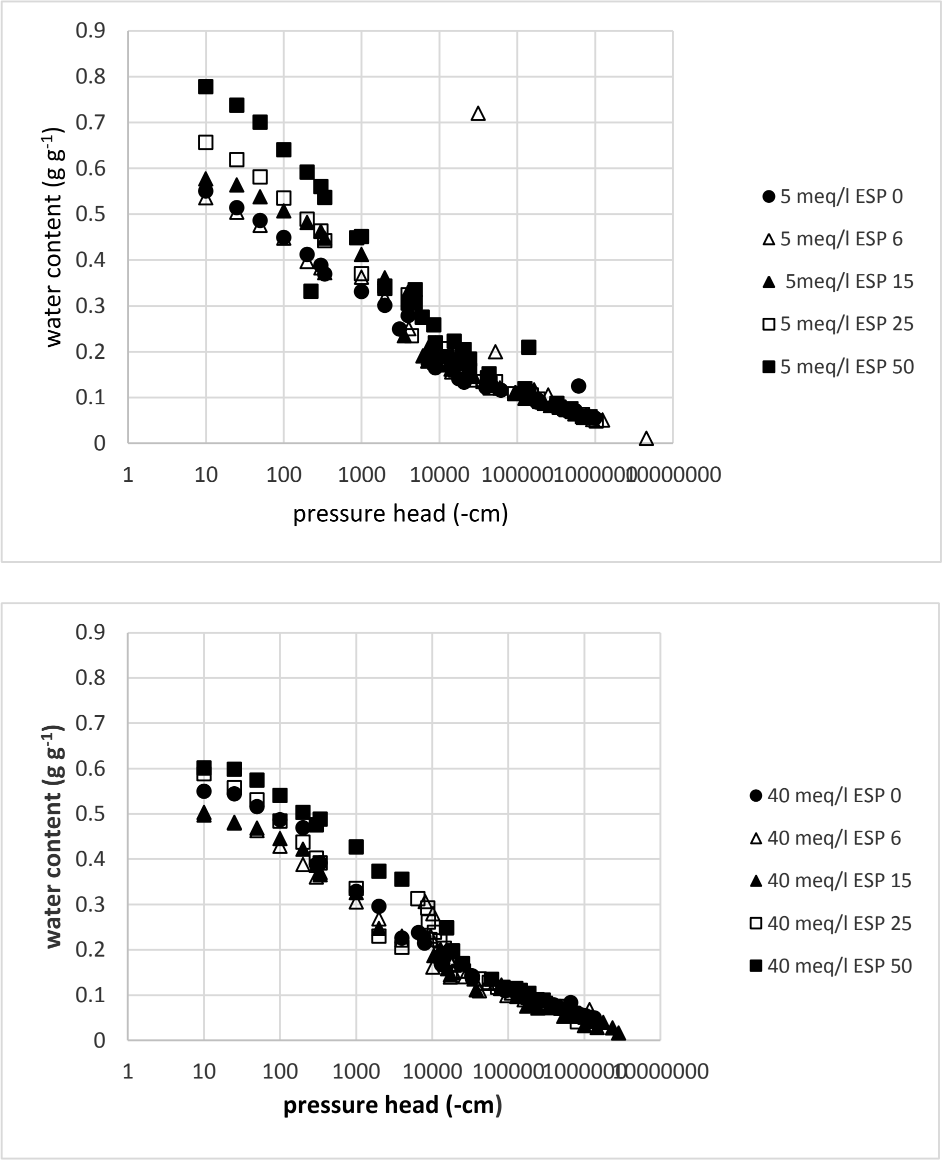


Figure 4. Water retention curves for the Exline soil at salt concentrations of 5 and 40 meq l^{-1} at different exchangeable sodium percentages (ESP).

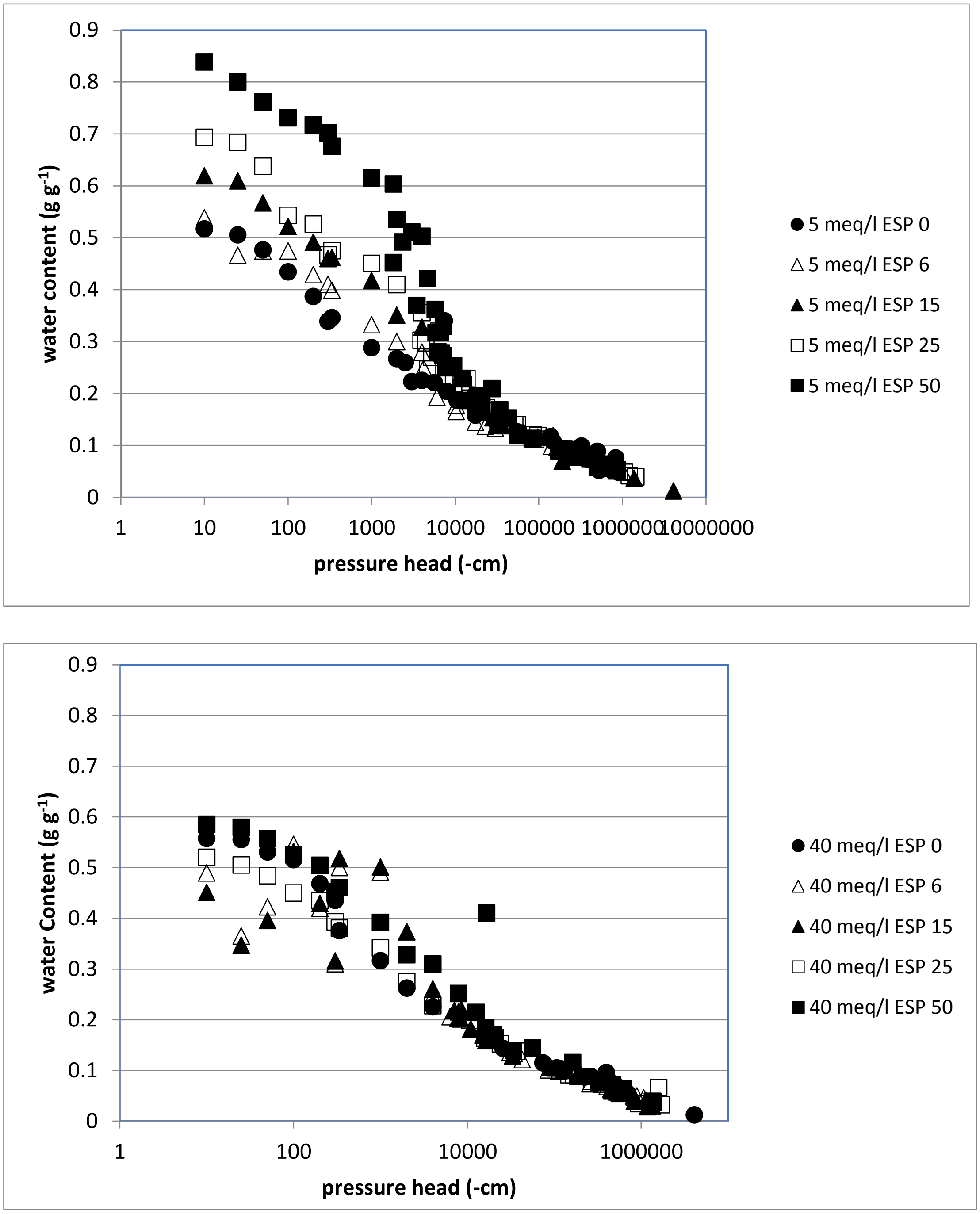
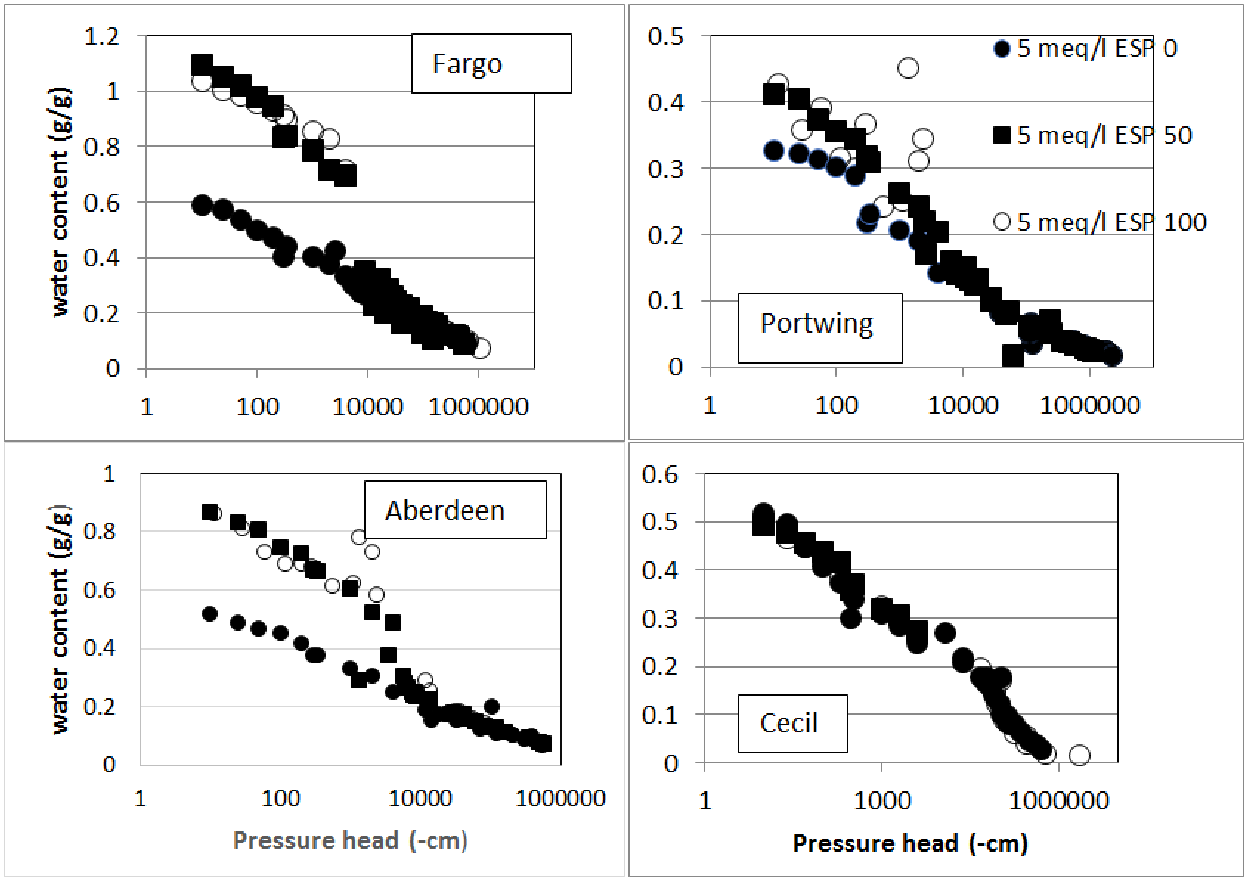


Figure 5. Water retention curves for the Harmony soil at salt concentrations of 5 and 40 meq l^{-1} at different exchangeable sodium percentages (ESP).

Figure 6. Water retention curves for Fargo, Aberdeen, Portwing and Cecil soils under ESP levels of 0, 50 and 100 % at a 5 meq l^{-1} electrical conductivity (EC) level.



Chapter 4. Prediction of Soil Hydrologic Properties on Salt and Sodium Affected Soils

Abstract

Soil hydraulic properties are important in managing soil salinity and sodicity with smectitic soils being most sensitive to soil solution composition. Many functions have been created to predict the hydraulic conductivity saturated soil (K_{sat}) and the soil water retention curve from soil texture, bulk density and other soil physical properties. These functions other than the McNeal function do not account for soil clay types or soil solution composition. The objectives of this study were to: 1) analyze the performance of previously developed pedotransfer functions (PTFs), 2) predict soil hydrologic properties on saline and sodic soils of differing mineralogy and 3) create PTFs that account for clay mineralogy and solution composition. Most previously developed PTF perform best on soils assigned to the mixed-active mineralogical and cation exchange activity class[4] than on soils classified as smectitic but over-estimates K_{sat} and under estimates soil water retention on smectitc soils. Accounting for soil CEC and solution composition should improve the prediction of K_{sat} and water retention on saline and sodic soils.

Introduction

Soil hydrologic properties are important for irrigation management, because salinity and sodicity management are coupled to soil water management. High soil exchangeable sodium percentage (ESP) and low soil salinity tend to decrease soil saturated hydrologic conductivity K_{sat} and increases soil water retention (McNeal et al., 1966). All the widely used functions for predicting soil hydrologic properties use soil particle size distribution and bulk density but do not account for changes of soil hydrologic properties by differences in electrical conductivity (EC)

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[4] The US Soil Taxonomy recognizes a number of classes with cation-exchange activity and mineralogy being two of many. Mixed and smectitic refer to mineralogical classes while active and superactive refer to cation-exchange activity classes.

and sodium adsorption ratio (SAR) (Schapp et al., 1998). Measuring soil hydrologic properties is time consuming and soil properties can widely vary spatially therefore PTFs that predict soil hydrologic properties can be useful in determining hydrology on a larger scale (Bouma, 1989).

McNeal et al., (1966) measured (K_{sat}) on a variety of soils from the Southwestern United States and found that soils containing greater amounts of smectite clay responded with a greater decrease in the soil K_{sat} when the solution EC decreased, and SAR increased. McNeal et al., (1968b) then created a function to predict the changes in soil K_{sat} based upon the swelling of a sodium-saturated Wyoming bentonite (Norrish, 1954). McNeal’s model includes soil salt concentration, ESP, the mass fraction of smectite, and a swelling constant of montmorillonite based upon the swelling data from Norrish (1954) and two soil specific fitting parameters to predict changes in saturated hydraulic conductivity.

Lagerwerff et al., (1969) introduced a new function to predict K_{sat} based upon the response of effective soil porosity to a diffuse double-layer model of smectite clay swelling. The change in swelling was related to solution composition with high SAR and low ESP leading to the greatest increase in soil swelling. This function requires ESP, the surface area of the soil and two empirical fitting constants. Minasny and McBratney, (2000) and Ajuha et al. (1984) introduced functions to predict K_{sat} using porosity and the soil water content at -1/3rd bar to predict the soil K_{sat}.

Suarez and Simunek,. (1997) used linear regression to represent changes in K_{sat} with pH, modifying the McNeal, (1968b) model to account for the effect of alkalinity on clay dispersion and hydraulic conductivity. This modified McNeal function appears as a module in Hydrus software to simulate changes in hydraulic conductivity in response to solution composition. The

McNeal module in Hydrus no longer asks the user to estimate the smectite clay content using x-ray diffraction and, instead assumes all soils contain 10% smectite by mass.

Ezlit et al., (2013) recently modified the McNeal, (1968b) model by adding an empirical constant to predict for the percent smectite and to account for dispersion instead of getting % smectite from X-ray diffraction. This model has more fitting parameters that needed to fix the hydraulic conductivity of an individual soil, decreasing its usefulness on soil with a range of textures and clay mineralogy.

An entirely different approach relies on PTFs to predict soil hydrologic properties by correlating them to basic soil characterization properties (Bouma, 1989). Some of the efforts using this approach use PTFs to predict parameters for the Kozeny equation (Millington and Quirk, 1960 and Marshall, 1957). The Kozeny equation predicts K_{sat} based on soil porosity and pore radius. Soils were also found to have differed hydraulic conductivities due to soil particle size distribution with Li et al., (1976) as the first attempt to predict K_{sat} using soil particle size classes.

Fractal theory is another technique used to predict soil hydrologic properties. This theory assumes the soil is separated into different particle size fractions with a characteristic pore size associated with each particle diameter (Arya and Paris, 1981). In this approach the soil is assumed to behave as a bundle of capillary tubes of different pore sizes that drain when the head becomes negative enough based upon capillary rise. This class of models does not account for swelling smectite clays but performed satisfactory on the soils ranging from sand to silty clay texture (Tyler and Wheatcraft, 1989)

Pedotransfer functions using multiple regressions are the most widely used. Soil hydrologic properties are estimated based upon easily measured soil chemical or physical properties available in a soil survey. The fewest the number of properties used in the function the easier it is to implement and predict the function of interest. Neural network analysis has been used to create many PTFs by expanding the dataset using the bootstrap method (Schaap et al., 1998). Most of the properties that PTFs are based upon are common soil characterization measurements such as particle sizes or bulk density, although some have used properties that are less readily available such as percent smectite or specific surface area (Klopp, 2015 and Lagerweff et al., 1969).

The most common single property to predict K_{sat} is clay content. A summary of properties used to predict K_{sat} such as dry bulk density, porosity or water retention points are listed in Table 1 (Puckett et al., 1984; Dane and Puckett, 1994; Schaap et al., 1998; Ajuha et al., 1984). None of the functions account for soil clay type or solution composition besides the Rosetta functions that includes water retention points in the prediction functions for soil properties. Expansive soils are soils where the volume of the clay fraction increases from wetting changing bulk density and pore sizes (Tuller and Or, 2003). Current PTFs do not account for the effect of soil clay type on the soil water retention curve.

Pedotransfer functions to predict soil physical properties are usually generated and validated using soils from a certain geographic area (Ajuha et al., 1984). Many of these PTFs perform poorly when they used to predict the hydraulic conductivity of soils from different geographic areas (Minasny and McBrantney, 2000). Pedotransfer functions such as the Hypres (Wösten et al, 1999) function was calibrated on samples from across Europe; the Rosetta PTF was generated from soils found in the UNSODA database.

The Rosetta-based PTFs have different levels of known characterization data that can be used to predict the van Genuchthen fitting parameters from particle size class, to particle size distribution with bulk density, There also is an ability to add -1/3rd and -15 bar water retention points to the PTF to predict soil water retention curve and K_{sat} (Schapp et al., 1998). Pedotransfer functions also have been created to have different functions for different particle size classes and different activities of clay minerals (Gaiser et al., 2003 and Minasny and McBrantney, 2000).

The Rosetta PTF, predicting -1/3rd and – 15 bar water contents, is currently used by the US Natural Resource Conservation Service (NRCS) to predict soil hydrologic properties. Hydrus 1-D also uses the Rosetta PTF to predict soil hydrologic properties and uses textural class, soil separates (sand, silt, and clay) bulk, density, -1/3rd and -15 bar water contents depending upon data available to the researcher. The modified[5] McNeal model used by Hydrus 1-D to predict changes in hydraulic conductivity in response to solution composition (Simunez and Suarez, 1997). Many other pedotransfer functions are available but little is known about how these functions perform on soils that are saline or sodic.

The earliest semi-empirical water retention models used soil particle class to predict the exponent of a Campbell power function (Clapp and Hornberger, 1978). Gupta and Larson (1979) and Rauls and Brakensiek, (1982) developed PTFs to predict several points on the water retention curve. This approach required many regressions run to get a soil water retention curve.

Vereecken et al., (1989) was the first to develop a PTF that predicted parameters for the van Genucthen function. Schapp et al., (1998) subsequently developed a PTF to predict van Genuchthen parameters and K_{sat} using neural network analysis on soils across the United States.

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[5] which assumes all soil contain 10% smectite

Wosten et al., (1999) introduced a PTF designed to predict soil hydrologic properties in Europe. Gaiser et al., (2003) developed a PTF to predict the negative third and -15 bar water content for high and low cation-exchange activity Brazilian soils. Most PTFs have a mixture of dominant soil clay types included in the prediction part of the model and do not account for the effects of clay type on the soil water retention curve. The performance of PTFs on soils with swelling smectite clays with a range of EC and ESP is unknown (Gaiser et al., 2000).

Objectives

The objectives of this work were to analyze how previously developed PTFs to predict K_{sat} and the soil water retention curve perform on saline and sodic soils, and whether clay mineralogy influences the performance of these equations. A second objective was to develop a PTF to predict K_{sat} on saline and sodic soils that accounts for the activity of the clays. Thirdly a PTF was developed to predict the water retention curve on salt affected soils and account for the activity of the clays.

Methods

Experimental Water Retention and Hydraulic Conductivity Data.

Water retention curves and K_{sat} were measured on two data sets of soils that differed in textures and soil mineralogy. The first data set had soil textures ranging between sandy loam and silty clay with clay content ranging from 16 to 53 %, bulk density values between 0.9 and 1.3 g cm^3, smectitic clay mineralogy classes and mixed active cation exchange activity class. The detailed soil characterization information is available in Appendix Table 1 of this chapter.

Soils were treated to EC levels between 0.5 and 8 dS m^{-1} and SAR values between 0 and 20. The hydraulic conductivity of saturated soil was measured on repacked cores using a constant approach (Reynolds et al., 2002). Water retention was measured at the same solution levels using the WP4 Dewpoint Potentiometer (Meter Group, Pullman WA), pressure plates and evaporation methods (Schindler et al., 2010, Dane and Hopmans, 2002). Water retention curves were fit with the van Genucthen constrained function with θ_s being the initial volumetric water content of saturated soil and $\theta_r=0$ being the residual soil moisture content (van Genuchthen, 1980)

Data from Chapter 3 has soil clay contents ranging between 25 and 50 percent clay, mineralogy of smectitic, mixed active and kaolinitic, with bulk density of the samples ranging between 1.05 and 1.25 g cm^{-3}. K_{sat} was measured using the constant head method at salinity levels between 5 and 40 $mmol^+ L^{-1}$ EC (0.6- 4.5ds m^{-1}) and ESP values between 0 and 25 (Reynolds et al., 2002). Water retention curves were measured using a tension table, pressure plates and Wp4 C data between 5 and 40 $mmol_c l^{-1}$, EC (0.6- 4.5ds m^{-1}) and ESP levels of 0 to 100 (Decagon Devices Inc, 2014 and Dane and Hopmans, 2002). Water retention curves were fit with the van Genucthen constrained function with being the initial water content at the start of measurement of the soil water retention curve and $\theta_r=0$ (van Genucthen, 1980) The combination of the data from chapter 3 and data from Klopp 2015 for SAR 0 and SAR 20 treatments were combined to make the prediction data.

Assessment of PTFs

The percent smectite required by the McNeal function was measured by X-ray diffraction peak intensity in the Klopp-(2015) data set. The percent smectite of the remaining soil is assumed to be 10%, which Suarez and Simunek (1997) argue is a reasonable assumption for many soils. No pH effect was included because all the studies used chloride salts. For the literature verification data for K_{sat} SAR was converted to ESP using the relationship from the US

Salinity Laboratory (USDA Handbook 60). The literature verification data consisted of data from (Chaudhari, 2001, Chiang et al., 1987 and Shainberg et al., 1981).

The geometric mean error (GMER) was calculated by equation (1a) where K_{sat}^{p} is the predicted and $K_{sat}^{m}$is the measured saturated hydraulic conductivity in cm day^{-1} and n is the number of samples.

$$ln(GRSS) = \frac{1}{n}\sum_{i=1}^{n}(\ln(K_{sat}^{p}) - \ln(K_{sat}^{m}))^2 \qquad (1a)$$

$$GMER = exp\left(ln(GRSS)\right) \qquad (1b)$$

The geometric root mean square error (GMRSE) ratio was calculated using equation 2 where GMRSE is the geometric root mean square error ratio.

$$ln(GMRMSE) = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\ln(K_{sat}^{p}) - \ln(K_{sat}^{m})\right)^2} \qquad (2a)$$

$$GMRMSE = exp\left(ln(GMRMSE)\right) \qquad (2b)$$

The R^2 value of each PTF was determined by GMRMSE (2b). The hydraulic conductivity functions analyzed are listed in Table 1 with the properties they used for their prediction. The functions were analyzed using the same databased used to create the hydraulic conductivity model.

Soil water retention curves were predicted using the soil physical properties that were available to predict the soil water characteristic curves. Water retention was predicted for the soil volumetric water content at -1/3 and -15 bar water contents using the Gaiser et al., (2000), Gupta and Larson, (1979) and Rauls and Brakensiek, (1982) models. Water retention curves were predicted using the van Genuchthen function with m=1-1/2n for the Vereecken et al., (1989) function (van Genucthen, 1980). For the two Rosetta, Hypres (Wösten et al, 1999), and Weynants et al., (2009) water retention PTF predict van Genuchten 1980 parameters with m=1-1/n. Soil properties used to predict soil water retention curves are listed in Table 4. Performance of the water retention functions were analyzed using root mean square error calculated by the following equation. Where θ_p is the predicted water content from the PTF and θ_m is the measured volumetric water content of

$$SSE = \sum_{i=1}^{N}(\theta_p - \theta_m)^2 \qquad (3)$$

$$RMSE = \sqrt{\frac{1}{n}SSE} \qquad (4)$$

$$Bias = \frac{1}{n}\sum_{i=1}^{N}(\theta_p - \theta_m) \qquad (5)$$

the soil at a given matric potential, SSE is sum of squared errors and Bias is the mean error of the PTF function.

Generation of New Saturated Hydraulic Conductivity PTFs

The PTF created for this thesis used all K_{sat} data from Chapter 3 and K_{sat} data for SAR 0 and 20 treatments from Klopp (2015). The initial PTFs used a single soil property, adding more soil properties incrementally to improve performance including: CEC7[6], sand content, EC, SAR and bulk density (ρ_b). Pedotransfer parameters were optimized by minimizing the geometric sum of squared errors (GMSSE) in equation (7b) The effectiveness of the function was verified on the SAR 3, 6 and 12 treatments from the Klopp (2015) dataset.

$$ln(GMSSE) = \sum_{i=1}^{N}(\ln\left(K_{sat}^{p}\right) - \ln K_{sat}^{m})^2 \qquad (7a)$$

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[6] cation exchange capacity measured using 1M ammonium acetate buffered at pH 7

$$GMSSE = exp\left(ln(GMSSE)\right) \qquad (7b)$$

The effectiveness of the PTFs was also verified on an independent K_{sat} dataset that included kaolinitic to smectitic clays and soil textures from sandy loam to clay (Chaudhari 2001, Chiang et al, 1987 and Shainberg et al., 1981). All data were pooled together, with 75 % of the data to generate the PTF and the other 25 % of the data to validate the PTF. The properties used for this function were sand, clay, CEC and ρ_b and EC, SAR, sand, clay, CEC and ρ_b

A separate PTF was created to predict the change in K_{sat} in response to solution EC and SAR. The relative hydraulic conductivity K_{rel} (8) compared to the highest salt level and lowest SAR treatment measured on a soil by equation (8), where the K_{sat}^{m} is the measured K_{sat} for a given SAR and EC combination. The K_{sat}^{r} is the average measured K_{sat} for the highest EC and lowest SAR combination for a given soil treatment.

$$K_{rel} = K_{sat}^{m}/K_{sat}^{r} \qquad (8)$$

The natural logarithm of the K_{rel} was predicted using solution EC, SAR, soil clay percentage and COLE in multiple regression by minimizing SSE of (ln(K_{rel}^{p})- ln(K_{rel})).^{2}. The GMRMSE, GMSE and R^2 of these regressions on predicted K_{sat} were analyzed on the same data sets as first set of K_{sat} equations. The predicted K_{rel} was multiplied times the K_{sat}^{r} data for the Klopp (2015) and literature verification data.

Generation of New Water Retention PTFs

Parameters for the van Genuchthen function (saturated gravimetric water content (w_s), alpha (α) and n values) can be predicted by a series of PTFs. The initial PTF was generated using: clay percentage and soil gravimetric water content at -1/3rd bar ($w_{1/3}$) by minimizing SSE of the predicted-fitted parameters from equation 3. A series of revised PTFs were then generated by adding the following properties: CEC, sand content, EC and SAR. The residual water content w_r was assumed to be zero. Gravimetric water contents (w) were used instead of volumetric water content to reduce the effect of volume changes caused by excessive swelling of some of the treatments when wetted.

$$\frac{w - w_r}{w_s - w_r} = S_e = \frac{1}{[1 + (\alpha|h|^n)]^m} \tag{9}$$

$$m = 1 - \frac{1}{n} \tag{10}$$

The version of the van Genuchten equation using gravimetric soil water content appears in equation (9) where w_s is the gravimetric water content of saturated soil, w_r is the residual water content (assumed to be zero), α is the inverse of the air entry potential and n is the pore size fitting parameter.

Water contents at a given matric potential were then predicted for the SAR 3, 6 and 12 treatments from the Klopp (2015) dataset and much larger soil survey characterization data for all soils from natric great groups (NRCS Soil Survey Characterization Database, 2019). The natric great groups data contained all horizons from A through C horizons, RMSE, Bias and R^2 of the predicted gravimetric water content was calculated for the two verification data sets.

Results

The best previously published function to predict K_{sat} on salt affected soil is the McNeal model (1968b) which predicted the K_{sat} with a GRMSR of 4.5 and a GMRE of 2.12 cm day^{-1} (Figure 1 and Table 3). The Brakensiek et al. (1984) model had the lowest GMRMSE and best GMSE of functions that did not require a reference measurement of K_{sat} (Figure 1). Most of the PTFs performed best on the mixed active cation-exchange activity class and worst on the smectitic clay mineralogy class soils (Appendix Table 4). The McNeal function performed best on the mixed active clay and kaolinitic soils, which had the least change in their K_{sat} as EC decreased and SAR increased. The Rosetta-2 PTF had the highest R^2 value of the PTFs although it had a GMRMSR of 12.5 and GMER of 5 cm day^{-1} (Table 2)[7].

Performance of New Hydraulic Conductivity PTFs

Equation A (Appendix Table 5 and Figure 4) using percent clay was able to explain 79 % of the variation in the Klopp 2015 data and 53 % on the other literature data although there was a GMRMSE of 5.98 and 5.62 cm day^{-1} for the two data sets respectively. Accounting for the CEC normalized clay content, sand content, solution EC and SAR reduced the GMRMSE to 3.14 and 5.4 cm day^{-1} as is shown by equation (11) following (function H, Appendix Table 5).

$$\ln(Ksat) = 2.09 - 0.036 * \frac{clay * CEC}{clay} + 0.057 * sand + 0.205 * EC - 0.16 * SAR \tag{11}$$

Equation 11 (cf. function H, Appendix Table 5) predicted K_{sat} at 6 % of geometric mean of the Klopp 2015 verification data and within 54 % of the measured value on literature data. Combining the literature data with the validation and prediction data using soil bulk density, CEC, clay content, sand content and solution SAR predicted the soil K_{sat} with a GMRMSE of 3.28 cm day^{-1} which is function (12) following (cf. function K, Appendix Table 5).

$$\ln(K_{sat}) = 5.17 - 0.054 * \frac{clay * CEC}{clay} + 0.052 * sand + 2.1 * \rho_b + 0.17 * EC - 0.093 * SAR \tag{12}$$

This GMRMSE was within 27% of the geometric mean of the random 25 % of total data that was used as verification data.

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[7] A GMER of greater than 1 means the function over predicts the value whereas a value less than 1 means the function under predicts K_{sat}.

Predicting the relative hydraulic conductivity K_{rel} using multiple regression was similar in GMRMSE of prediction data compared to McNeals domain model. The GMRMSE using multiple regression function equation (13) following and function I, (Appendix Table 6) was 1.93 and 4.34 cm day^{-1} for the Klopp (2015) and literature data sets respectively compared to 1.81 and 5.2 cm day^{-1} using the McNeal model respectively (Table 3).

$$\ln Krel = 0.023 * EC - 0.143 * SAR \tag{13}$$

The GMER values of 0.99 and 0.97 cm day^{-1} compared to 1.31 and 1.76 cm day^{-1} for function (13) (cf. function L, Appendix Table 6) versus the McNeal hydraulic conductivity function respectively (Figure 1 and Figure 4). This means the model predicted the K_{sat} closer to the measured data for both data sets from a simple regression function. Adding clay percentage to this function (expression (14)) further reduced the GMRMSE to closer to the McNeal model. Adding cation exchange capacity improved the prediction of K_{rel} using the Klopp-2015 dataset but performed worse on the literature validation dataset (PTF M, Appendix Table 6).

$$\ln Krel = 0.000215 * EC * clay - 0.00341 * SAR * clay \tag{14}$$

$$\ln Ksat = 9.5 - 0.059 * \frac{clay * CEC}{clay} + 0.067 * sand + 2.1 - 6.0 * \rho_b \tag{15}$$

Pedotransfer function (15)[8] performed poorly on the data that was independent of the Klopp 2015 dataset. Creating an equation to predict K_{sat} at high EC low SAR treatment and K relative relationship did not reduce the GMRMSE compared to PTF (12) when there was an unknown reference K_{sat} at a high ESP value.

Performance of Previously Developed Water Retention PTFs

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[8] cf. Pedotransfer function J, Appendix Table 5

All previous water retention PTFs predicted water retention curves with RMSE values between 0.09 and 0.14 $cm^3\ cm^{-3}$ (Table 4). All PTFs that predicted van Genuchten fitting parameters consistently under predicted the soil water retention curves (Table 5 and Figure 3). The PTFs consistently under estimate water retention by high ESP, low EC smectitic soils above -1/3rd bar matric potential (Figure 3). Although the Rosetta-2 PTF, which includes the -1/3rd and -15 bar water contents, performed the best relative to other PTFs it did not fit the overall shape of the retention curve on the sandy loam soil and did not characterize the wet end of the soil water retention curve on smectitic soils, especially ones that had high ESP (Figure 3).

On the NCSS natric great group dataset the Rosetta PTFs was able to predict water retention curve points with an RMSE of 0.059 $cm^3\ cm^{-3}$ although 91 percent of the 2075 water retention points in the characterization data point set were at water potentials from -1/3rd bar to -15 bars (Figure 2). The NCSS natric great group dataset has few water retention data between saturation and -1/3rd bar, which is an important range of water retention for soil water and salt transport.

The Rosetta-2 PTF predicted water retention with an RMSE of 0.058 $cm^3\ cm^{-3}$ on the Klopp (2015) data in the range of -1/3rd to -15 bars but was much farther off at potentials greater than -1/3rd bar with an RMSE of 0.103 cm^3cm^{-3}. The PTFs other than the Rosetta-1 and Rosetta-2 PTFs made curves very similar to each other on loamy and fine textured soils, under predicting water retention on the wet end of the soil water retention curve and over predicting water retention on dry end of the water retention curve (Figure 3A and 3B)

All PTFs listed in Table 4 and 5 tended to predict their bias in the same way regardless of soil mineralogy with many of the functions under predicting the soil water retention (Table 6). The Hypres (Wösten et al, 1999), Vereecken (1989) and Weyants et al., (2009) PTFs all under predicted water retention regardless of soil mineralogy (Table 6). The Rosetta I and II PTFs worked the best overall regardless of mineralogy. All PTFs had the least bias and lowest RSME on soils with mixed clay types (Table 6) and specifically the mixed active cation-exchange activity class. Pedotransfer functions Rosetta-1 and Rosetta-2 performed better on the NCSS natric great group dataset and the Klopp 2015 dataset than prediction data although all of the verification data was measured between -100 and -15300 cm matric potential.

Newly Created Water Retention PTFs

I developed a PTF (cf. PTF A1, Appendix Table 7) that estimates van Genucthen parameters from clay percentage; 82% of the variation (R^2) was explained in the water retention data of the Klopp 2015 verification data and 47% of the variation of the data in the NCSS natric great group dataset respectively (PTF A1. Appendix Table 7). The RMSE was 0.089 and 0.1 g g^{-1} for these two data sets (PTF A1. Appendix Table 7).

A PTF based on water content at -1/3 bar as a parameter (PTF 16a-16c)[9] predicted van Genuchthen fitting parameters estimated the water retention curve with an RMSE of 0.042 and 0.059 g g^{-1} on Klopp 2015 and natric soil great group data respectively with R^2 values of 0.91 and 0.78, respectively (Figure 5). The individual PTFs to predict each of the van Genuchthen fitting parameters appear below.

$$w_s = 0.41 + 0.0075 * w_{\frac{1}{3}} \tag{16a}$$

$$\ln \alpha = -3.11 + 1.0 * w_{1/3} \tag{16b}$$

$$\ln N = 0.29 - 0.253 * w_{1/3} \tag{16c}$$

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[9] Cf. PTF A2, Appendix Table 7

$$w_{1/3} = 0.189 + 0.0072 * clay * \frac{CEC}{clay} + 0.0075 * \frac{SAR}{EC} - 0.00143 * sand \quad (17)$$

This is within 21 % and 26 % of the mean water contents of 0.191 and 0.221g g^{-1} for the Klopp and natric soil great group data set respectively. The performance of PTFs (16a-16c) and (17) is same as the Rosetta 2 PTF on the natric soil great groups (Table 6, column 4) and improved over the Rosetta 2 functions performance on the data to create this function. The soil water content at – 1/3rd bar can be predicted within 9% percent of the mean $w_{1/3}$ water content of 0.27 g g^{-1} on the Klopp 2015 data although it is within 37 % of the mean 1/3 bar water content on the Natric great group data. The RMSE is 0.025 g g^{-1} on Klopp (2015) data and 0.11 g g^{-1} on Natric soil survey great group data.

Accounting for solution composition in PTF (18 a)-(18c) with soil CEC, sand and clay content did not improve the RMSE or R^2 prediction of the prediction on either of the validation sets. The best function to predict Klopp 2015 data used sand, clay and CEC and for Natric soil great groups used percent clay and 1/3rd bar water content (Appendix Table 7).

$$w_s = 0.671 + 0.0011 * clay + 0.0043 * CEC - 0.00396 * sand - 0.00239 * EC + 0.0024 * SAR \quad (18a)$$

$$\ln \alpha = -2.8 - 0.030 * clay + 0.056 * CEC - 0.012 * sand - 0.024 * EC + 0.0042 * SAR \quad (18b)$$

$$\ln N = 0.37 - 0.0023 * clay - 0.00385 * CEC + 8.5 * 10^{-5} * sand + 0.0017 * EC - 2.6 * 10^{-4} * SAR \quad (18c)$$

Discussion

Hydraulic Conductivity

This chapter evaluates two semi-empirical models designed to predict the effect of clay swelling on K_{sat} (Lagerwerff et al., 1969, McNeal, 1968b). The McNeal (1968b) model requires an estimate of soil smectite content based on quantitative X-ray diffraction (cf., McNeal, 1968a). The Largerwerff et al. (1969) model, which never gained acceptance as a practical hydraulic conductivity model, requires the soil specific surface area and relies on a simple diffuse double-layer model to represent clay swelling behavior.

Suarez and Simunek (1997) and Ezlit et al. (2013) modified the original McNeal (1968b) to be more like empirical PTFs, both abandon use of XRD to estimate the soil smectite clay percentage and assume all soils contain 10%[10]. Assuming the smectite content is 10% is acceptable if the soil is loam textured and classified as either mixed active or super active cation-exchange activity class. For example a soil with 20 % clay with a CEC of 14 cmol kg^{-1} the assumption of 10% would be reasonable, but not if a soil has clay contents less than 10 % or in fine textured soils > (30 % clay) with a mixed super active cation-exchange activity class or smectitic mineralogy class.

The Ezlit model abandons any attempt to quantify the smectite content and, instead, fits the empirical relative hydraulic conductivity curve of each individual soil. As a result, model parameters are specific to each soil in their study. Statistical regression functions relating soil hydrological properties to data such as available in a soil surveys are useful for predicting soil hydrologic properties on a landscape basis and the functions are more versatile on a variety of data sets.

Most hydraulic conductivity PTFs (Table 1) use particle size distribution and soil porosity or bulk density, ignoring both soil clay types and solution composition. Furthermore,

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[10] MnNeal (1968b) recommended a default 10% smectite content if the smectite content was unknow.

none of these PTFs were generated using data from smectitic soils. The Puckett et al., (1985), Dane and Puckett, (1994) and Campbell and Shiozawa, (1994) models were all generated using kaolinitic and siliceous soils from the Southeastern US. Not surprisingly, all perform poorly on the soils used in this dataset. The Cosby et al., (1984) created from soils from 22 states in the United States performed the worst of all the PTFs although the performance of the functions was worst in smectitic clay mineralogy soils (Appendix Table 3 and Appendix Table 4)).

Rosetta-1 and Rosetta PTFs (Schapp et al., 1998) were created with data from the UNSODA database, Minamasy and McBrantley, (2000) used soils from Australia and Hypres (Wösten et al., 1999) PTFs used soils from Europe of a range of clay mineralogy. These PTFs developed on soils of a mixture of clay types predicted hydraulic conductivity best on soils classified as mixed-active cation-exchange activity and worst on the smectitic mineralogy class soils. This would be expected because smectitic soils have larger changes in K_{sat} from SAR by EC combination and have lower K_{sat} compared to mixed active cation-exchange activity class and kaolinitic mineralogy class soils. All these models created on soils of a range of clay mineralogy overestimated the K_{sat} on the dataset of primarily smectite clay-based soils although some of the functions under predicted K_{sat} on this data set.

When using the McNeal (1968b) model to predict K_{sat} the prediction under EC and SAR combinations was better than when the PTFs listed in Tables.1 and 2. The Klopp 2015 had XRD quantified percent smectite available, whereas when predicting the K_{sat} of the literature data the smectite percentage was assumed to be 0.10. This may have been reasonable on the silt loam textured soil from Chaudhari (2001) but was likely an unreasonable estimate in the sandy loams or the clay soil. The McNeal model still predicted K_{sat} reasonably well although it preformed best on soils that were not smectitic and predicted a smaller K_{sat} under various EC and SAR.

Water Retention

Published PTFs to predict soil water retention were similar in the RMSE of predicting the soil water retention at a specific pressure head. All the PTFs to predict the van Genuchthen parameters used particle sizes, OM and bulk density as the prediction properties.

Not surprisingly, the Rosetta-2 PTF generated using -1/3rd bar and -15 bar water content performed well at water potentials between -1/3rd and -15 bars but consistently over predicted water content at water contents less than –15 bars and under predicted soil water content at potential greater than -1/3rd bar. The Rosetta-2 PTFs performed the best of the water retention curve PTFs evaluated here. All other water retention PTFs all performed poorly at water potentials greater than – 1/3rd bar. Water transport in soils at water potentials near saturation is important in characterizing salt and water transport and these prediction functions performed poorly in this range.

The water retention PTFs tended to preform best on mixed active cation-exchange activity soils and worst on smectitic soils besides the Gupta and Larson, (1979) and Gaiser et., (2000) PTFs. Including the soil water contents at -1/3 and -15 bars does account for the effect of clay type and solution composition and improved the prediction of the water retention curve using the Rosetta 2 PTF. The Rosetta 1 function performed like the Rosetta 2 function on mixed active and mixed semi-active soils but preformed worst on mixed superactive and smectitic soils. This is due to the PTFs not accounting for the effects of clay type, EC and SAR levels.

The new PTFs introduced in this chapter showed improved performance predicting soil water retention relative to previously developed PTFs when their performance was evaluated on soils containing high amounts of smectite clays. Adding water retention points improved prediction of the water retention curve compared to including textural and chemical properties of the soil. This was also found by others (Schaap et al., 1998, Rauls and Brakensiek, 1982).

The best models to predict the soil water retention for the NCSS natric great group dataset did not account for solution (EC, SAR) composition. This may be due to differences between wetting solutions used to measure water retention for the dataset, and wetting solutions used to measure water retention for the Klopp 2015 verification dataset.

The standard water -retention measurement procedure uses 0.005 M $CaSO_4$ to wet the soil (Dane and Hopmans, 2002). This wetting solution will result in water retention similar to a soil with a low SAR. The soil survey soils are likely wetted with tap water or standard calcium sulfate solution suggested in their methodology (Soil Survey Staff, 2014).

The natric great group data set had soils with a larger range of particle sizes compared to the prediction data set. The PTF using clay, sand and CEC worked best on Klopp (2015) data and function using the soil water content at -1/3rd bar and clay percentage predicted the water retention curves best on the soil survey data from sodic soils. The prediction of water retention in the greater than -1/3rd bar range was improved compared to PTFs from the literature. The prediction of 1/3rd bar water content on all soils did include the solution composition of the soil in the equation that worked best.

Conclusions

The McNeal and Lagerwerff models, which are not PTFs, were developed to predict changes in soil K_{sat} due to clay swelling in response EC and SAR. Both of these models are difficult to use because they require properties not routinely measured on soils. Alternatively, PTFs that reply on routinely measured soil properties consistently over predicted soil K_{sat} on smectitic soils and do not consider the effect of soil solution compositions on the soil. The functions developed in this work to estimate soil K_{sat} included CEC, saturated paste EC, and saturated paste SAR predicted K_{sat} with a smaller GMRMSE compared to previously developed PTFs. A simpler multiple regression equation we predicted the change in relative K_{sat} comparable to the McNeal model. This function does not require semi quantitative X-ray diffraction estimates of the smectite clay content to estimate the effect of EC and SAR on K_{rel}

Previously developed PTFs that do not include water retention points for estimating van Genuchthen parameters consistently under predicted soil water retention in smectitic soils. Previously published water retention PTFs consistently performed poorly when estimating the effect of EC and SAR on the wet end of the soil water retention curve, precisely the range critical to leaching of solutes and salt management. The PTFs generated in this study improved the prediction of the soil water retention curve and improved predictions over functions that did not use soil water retention points on soil survey characterization data.

Clay mineralogy and solution composition are clearly important for the prediction of soil hydrologic properties and should be included among the soil parameters commonly used by PTFs (i.e., soil particle size distribution, organic matter and bulk density).

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Tables and Figures

Tables

Table 1. Properties used to predict K_{sat} in PTFs. Sa is percent sand, Si is percent silt, OM is percent organic matter, Pb is bulk density in g cm^{-3}, -1/3rd bar and -15 bar are water contents at these two matric potentials in cm^3 cm^{-3}, ϕ_e is soil effective porosity in cm^3 cm^{-3}, T is top soil vs sub soil, and ϕ is porosity in cm^3 cm^{-3}

Function	Sa	SI	Cl	OM	Pb	-1/3rd bar	-15 bar	Φe	T	ϕ
Rosetta-1	X	X	X		X					
Rosetta-2	X	X	X		X	X	X			
Ahuja et al., 1984					X	X		X		
Campbell, 1985	X	X	X		X					
Campbell and Shiozawa, 1995	X		X							
Cosby et al., 1984	X		X							
Puckett et al., 1984			X							
Dane and Puckett, 1984			X							
Brakensiek et al., 1984	X		X							X
Saxon et al., 1986	X		X							
Tyler and Wheatcraft, 1989	X	X	X							X
Hypres (Wösten et al, 1999) (Wösten et al, 1999) (Wösten et al, 1999)		X	X	X	X				X	
Minasny and McBratney, 2000								X		

Table 2. Performance of functions to predict K_{sat} on soils with the geometric root mean squared error (GRRMSR) in cm day^{-1}, geometric mean error (GMER) in cm day^{-1}, and R^2 value of the prediction equation data set. All functions listed below are PTFs with the sole exception of McNeal and are were analyzed on data used to create the pedotransfer functions (1968b)

Equation	GRRMSR	GMER	R^2
McNeal, 1968b	4.58	2.12	0.68
Rosetta-1	11.5	3.7	0.75
Rosetta-2	12.5	5.0	0.77
Ahuja et al., 1984	8.99	2.92	0.37
Campbell, 1985	6.37	1.08	0.33
Campbell and Shiozawa, 1995	31.1	14.3	0.44
Cosby et al., 1984	1068.7	221	0.45
Puckett et al., 1984	86.8	0.026	0.051
Dane and Puckett, 1994	19.48	0.16	0.05
Brakensiek et al., 1984	6.04	0.87	0.32
Saxon et al., 1986	13	0.3	0.006
Tyler and Wheatcraft, 1989	21.2	7.9	0.032
Hypres (Wösten et al, 1999)	10.2	4.3	0.53
Minasny and McBratney, 2000	8.6	2.4	0.41

Table 3. Performance of functions to predict Ksat for soils on the verification data set. Not enough data was available to use the Rosetta 2 PTF on the Klopp 2015 and literature data. The GRRMSR is geometric root mean squared error in cm day^{-1} and GMER the geometric mean error in cm day^{-1}.

Equation	GRRMSR	GMER	GMRMSR literature data	GMER literature data
McNeal 1968	1.81	0.59	5.2	0.37
Rosetta-1	11.5	3.7	7.24	3.25
Rosetta-2	2.01	1.34		
Ahuja et al., 1984	3.82	3.24	8.56	1.16
Campbell, 1985	3.34	0.32	22.9	0.7
Campbell and Shiozawa, 1995	3.98	3.19	26.77	12.09
Cosby et al., 1984	22675	221	524903	288505
Puckett et al., 1984	189	0.007	28.0	0.07
Dane and Puckett, 1994	31.52	0.038	7.16	0.32
Brakensiek et al., 1984	3.03	1.84	7.1	0.74
Saxon et al., 1986	42.4	18.3	14.6	10.4
Hypres (Wösten et al, 1999)	1.9	0.54	271.7	0.005
Minasny and McBratney, 2000	1.95	0.95	18.82	1.79

Table 4. Soil properties used in PTFs to predict the soil water retention curve. Topsoil is considered to be a value of 1 and 0 for subsoil.

Equation	Sand (%)	Silt (%)	Clay (%)	Bulk Density (gcm^{-3})	Organic Matter (%)	CEC class	Topsoil	$1/3^{rd}$ Bar	15 bar
Rosetta I	X	X	X	X					
Rosetta II	X	X	X	X				X	X
Gupta and Larson, 1979	X	X	X	X	X				
Rauls and Brakensiek, 1985	X		X		X				
Vereecken et al., 1989	X		X	X	X				
Hypres (Wösten et al, 1999)		X	X	X	X		X		
Gaiser et al., 2000		X	X		X	X			
Weynants et al., 2009	X		X	X	X				

Table 5. Root mean square error, Bias and R^2 value of water retention curve prediction functions. The Gupta and Larson (1979), Rauls and Brakensiek (1982) and Gaiser et al., 2000 equations were used to predict 1/3rd and 15 bar water content. The other equations were used to predict van Genucthen fitting parameters and compared to measured data at the same potentials.

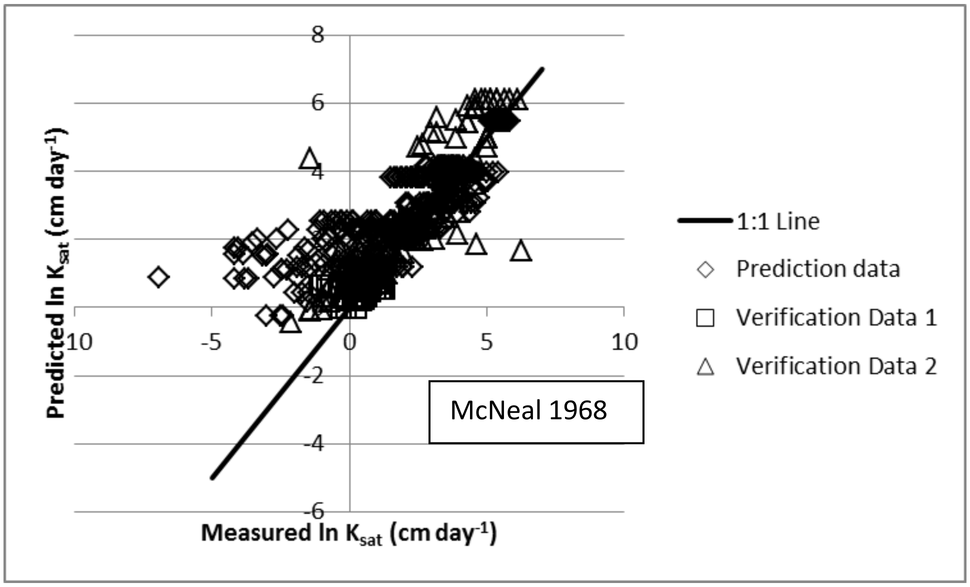
Equation	RMSE ($cm^3\ cm^{-3}$)	Bias ($cm^3\ cm^{-3}$)	R^2
Rosetta I	0.099	-0.081	0.836
Rosetta II	0.0919	-0.072	0.862
Gupta and Larson, 1979	0.096	0.043	0.341
Rauls and Brakensiek, 1982	0.097	0.029	0.315
Vereecken et al., 1989	0.138	-0.061	0.560
Hypres (Wösten et al, 1999)	0.0935	-0.051	0.691
Gaiser et al., 2000 Low activity clays	0.095	-0.044	0.28
Gaiser et al., 2000 High activity clays	0.089	-0.04	0.336
Weynants et al., 2009	0.115	-0.066	0.528

Table 6. Performance on water retention curves on soils of differing mineralogy and on the verification data sets with RMSE and bias (mean error) of the functions in ($cm^3\ cm^{-3}$). The numbers of water retention points in each category are in parenthesis.

Function		Rosetta I	Rosetta II	Gupta and Larson	Rauls and Brakensiek	Vereecken	Hypres (Wösten et al, 1999)	Gaiser et al., 2000 low CEC	Gaiser et al., 2000 High CEC/	Weyants
Smectitic	RMSE	0.102	0.083	0.12	0.091	0.146	0.094	0.114	0.095	0.111
(14644)	Bias	-0.077	-0.047	0.099	0.034	-0.05	-0.044	-0.062	-0.048	-0.054
Mixed Superactive	RMSE	0.035	0.038	0.11	0.10	0.144	0.125	0.135	0.124	0.106
(1355)	Bias	-0.014	0	0.095	0.011	-0.037	-0.038	-0.112	0.102	-0.015
Mixed active	RMSE	0.08	0.074	0.130	0.098	0.0885	0.078	0.114	0.097	0.100
(4243)	Bias	-0.001	-0.058	0.126	0.05	-0.051	-0.04	-0.073	-0.094	0.008
Mixed semiactive	RMSE	0.067	0.052	0.145	0.068	.158	0.194	0.103	0.066	0.109
(51)	Bias	-0.0035	0.008	0.125	-0.026	-0.079	-0.129	-0.090	-0.046	-0.023
Kaolinoitic	RMSE	0.097	0.089	0.136	0.058	0.149	0.083	0.063	0.045	0.108
(193)	Bias	-0.081	-0.082	0.135	0.04	-0.089	-0.003	-0.070	-0.024	-0.0633
Klopp 2015 data	RMSE	0.034	0.035	0.16	0.13	0.078	0.067	0.063	0.057	0.068
(1260)	Bias	-0.005	-0.19	0.13	0.1	0.044	0.058	0.024	0.015	0.06
Natric great group	RMSE	0.088	0.059	0.136	0.098	0.147	0.156	0.147	0.117	0.11
data (2569)	Bias	-0.035	0.025	0.036	-0.051	-0.046	-0.048	-0.124	-0.084	-0.025

Figures

Figure 1. Predicted vs Measured K_{sat} for the McNeal (1968), and Brakensiek et al., (1984) model. The GMRMSE was 1.75 and 3.03 (cm day^{-1}) for the verification data set 1 (Klopp 2015 data) and 3.46 and 7.1 (cm day^{-1}) for verification data set 2 (Literature data) for the McNeal, (1968) and Brakensiek et al., (1984) hydraulic conductivity prediction models respectively.



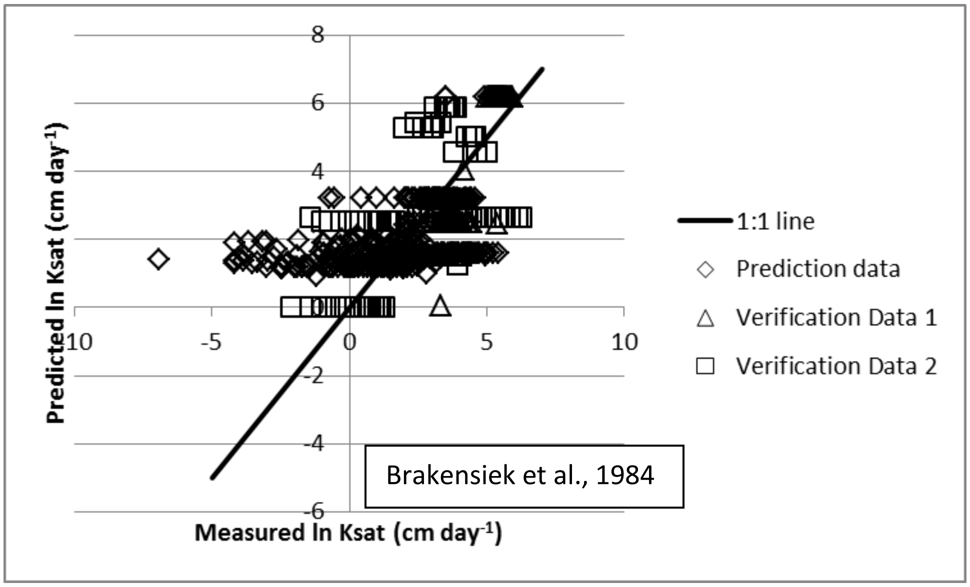
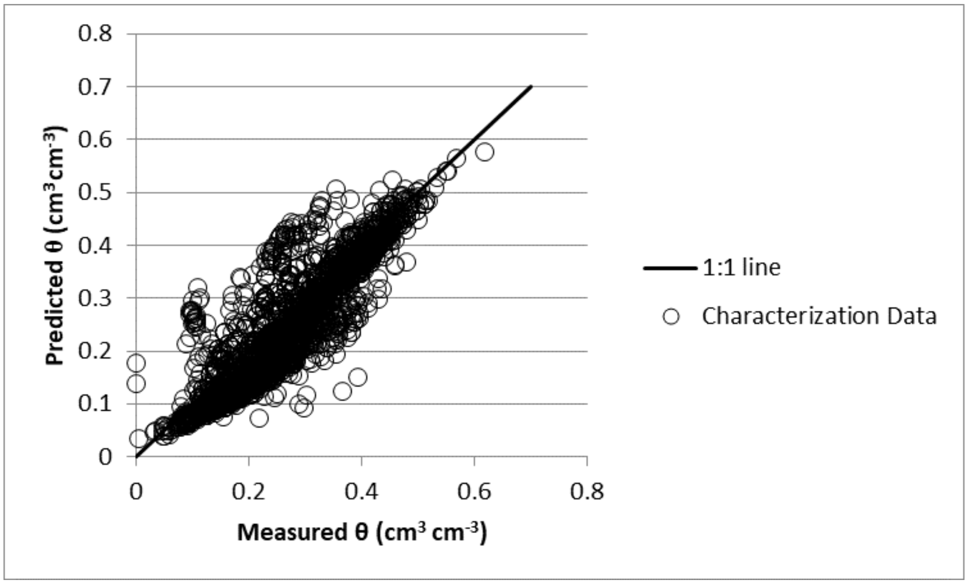


Figure 2. Measured versus predicted water contents using the Rosetta PTF on soil characterization data and the prediction data for the soil water characteristic curve.



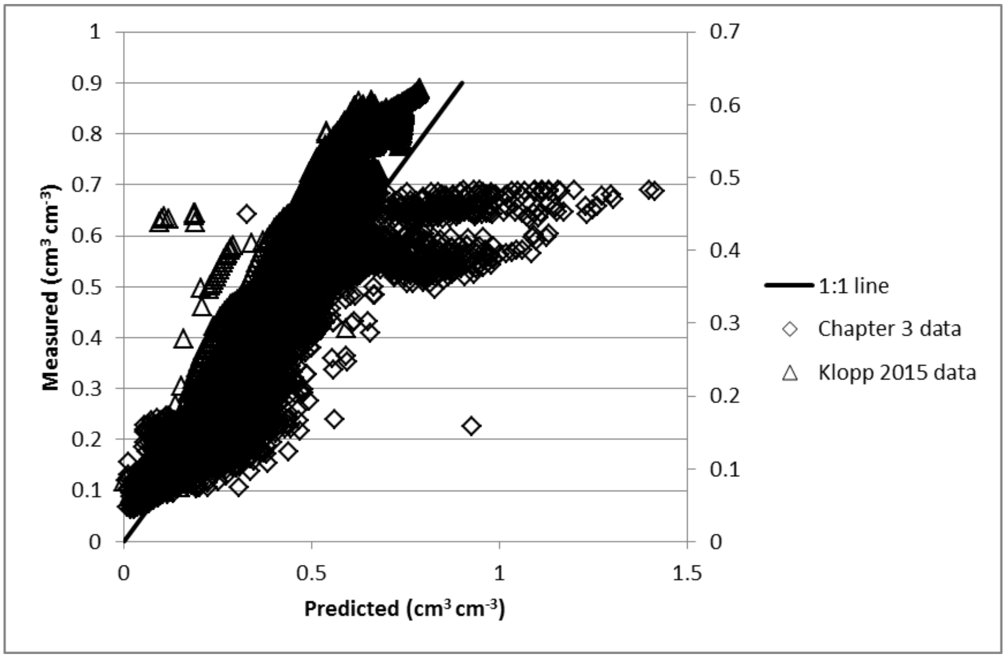
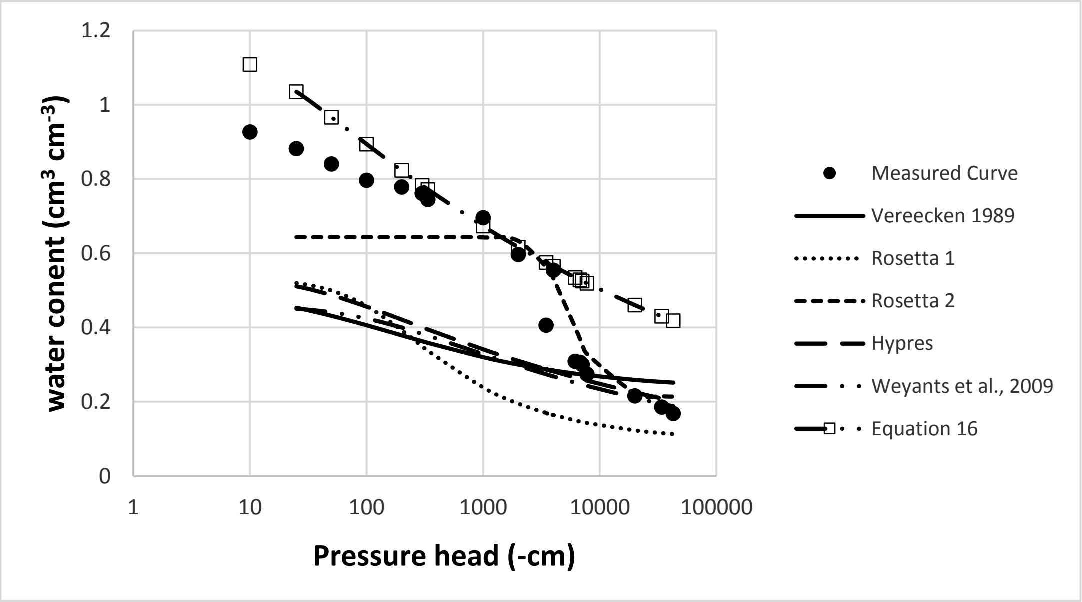


Figure 3. Measured water retention curves for (A) Harmony soil for the 5 meq l^{-1} ESP 50 treatment and (B) 1:2 Fargo Serden Mix for the 5 meq l^{-1} ESP 0 treatment.



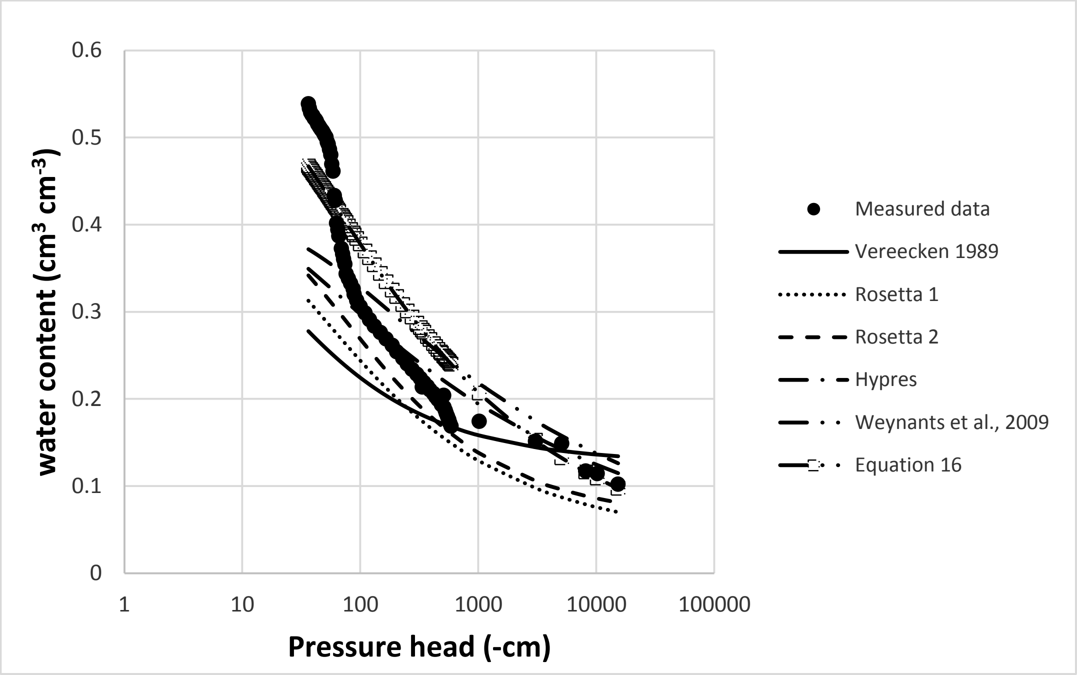

0.6
0.5
0.4
0.3
0.2
0.1
0
water content (cm³ cm⁻³)
1
10
100
1000
10000
100000
Pressure head (-cm)
Measured data
Vereecken 1989
Rosetta 1
Rosetta 2
Hypres
Weynants et al., 2009
Equation 16

Figure 4. Measured versus predicted K_{sat} for the created PTF equations, A, H, K and M. Equation A, H and M were verified on the Klopp (2015) and Literature data. Equation K used 75% of all data for creation and 25% of the data for verification.

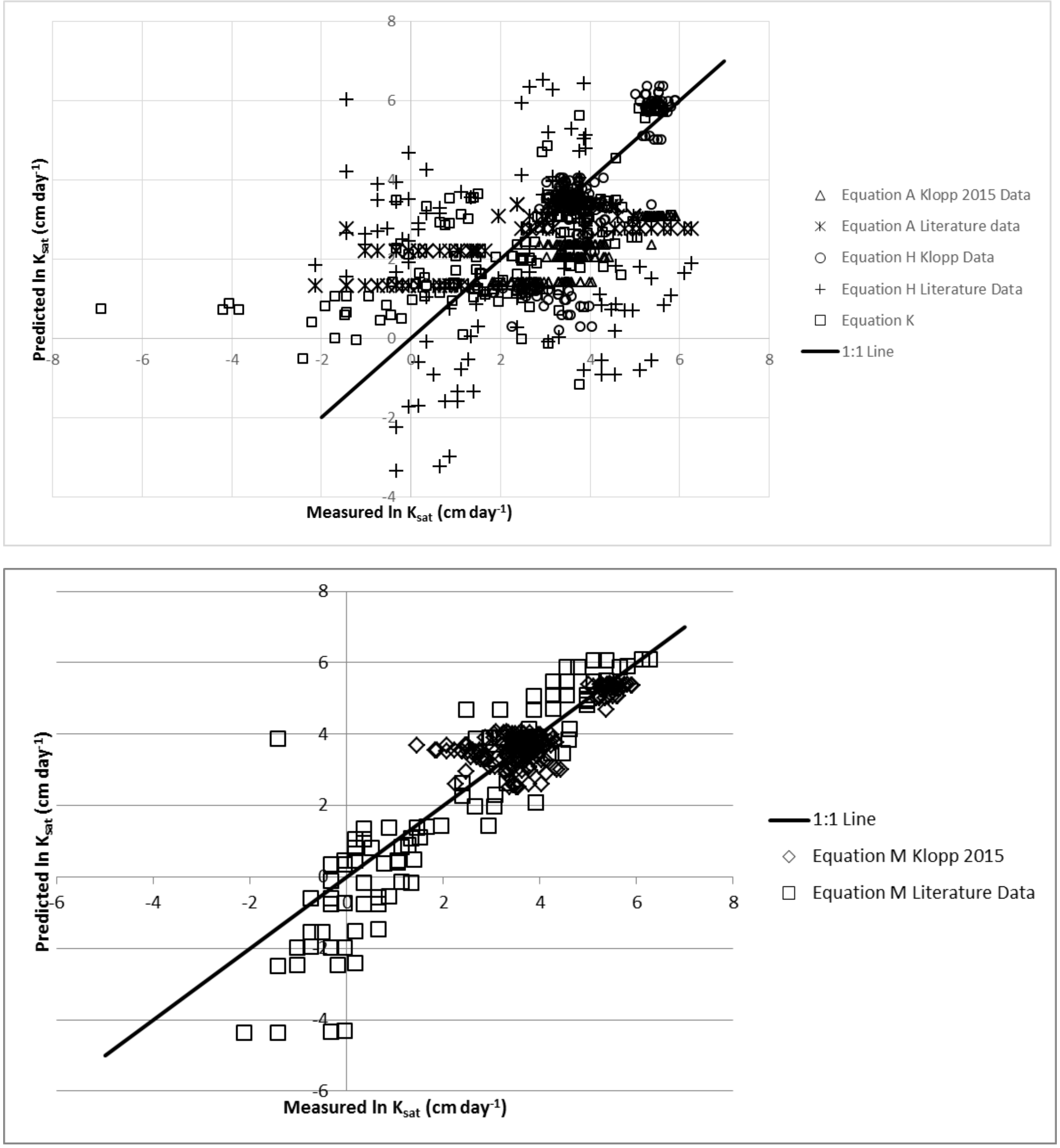
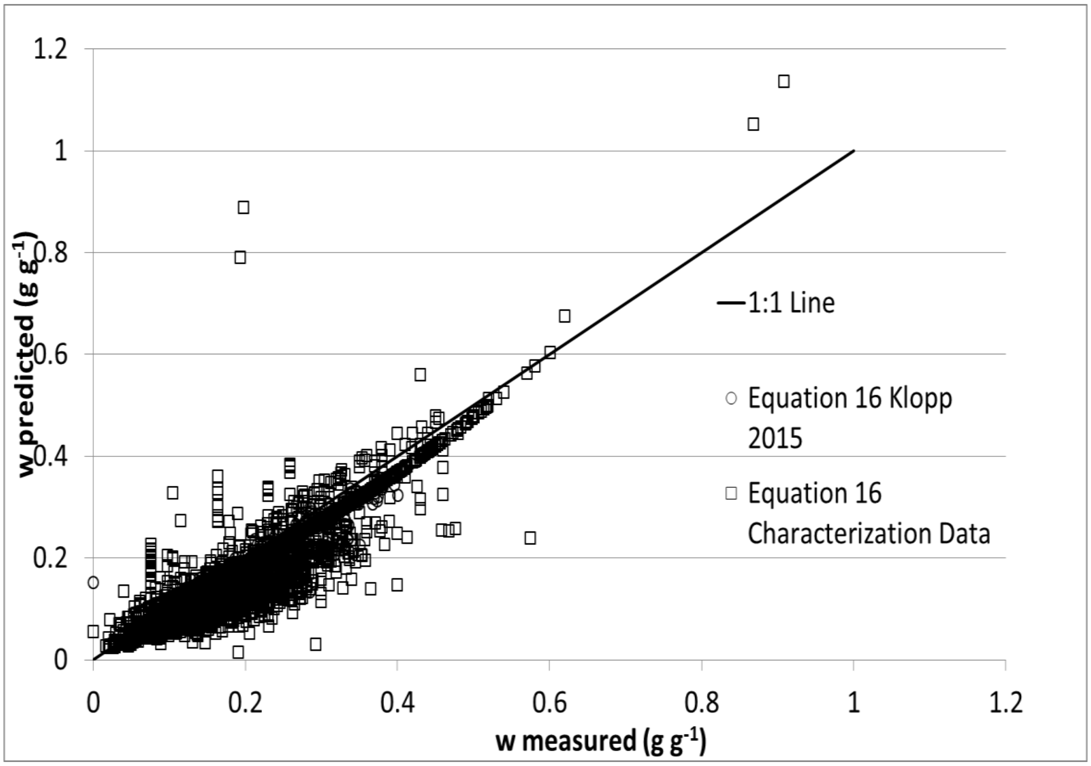
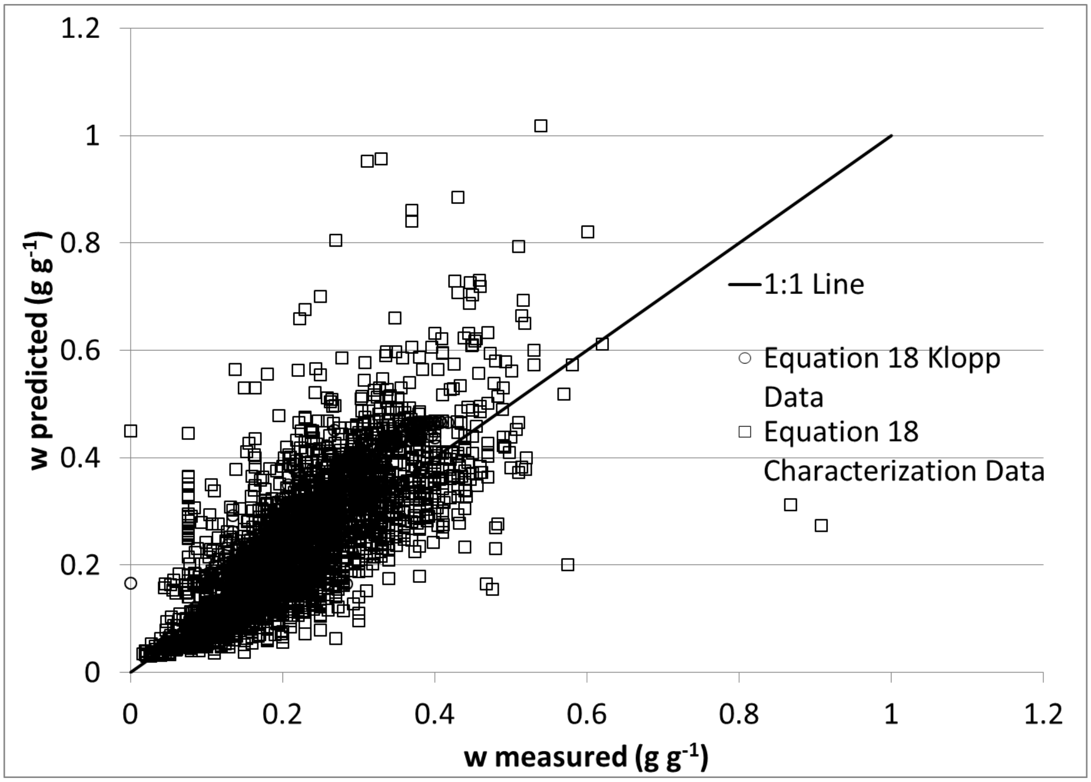


Figure 5. Measured versus predicted gravimetric water content estimated with equation 16 and 18 using data from Klopp 2015 and soil characterization data from sodic soils.





Appendix Tables.

Appendix Table 1. Particle size distribution, CEC using Ammonium Acetate pH 7 and mineralogy of soils used for prediction data and verification data set 1

Soil	Sand (%)	Silt (%)	Clay (%)	CEC $cmole_c$ kg^{-1}	Mineralogy
Cecil	24.3	25.7	50.0	10.1	Kaolinitic
Fargo	1.6	48.5	49.9	45	Smectitic and some Illite
Aberdeen	1.90	61.2	36.9	31	Smectitic and some Illite
Exline	3.10	61.4	35.5	25	Smectitic and Some Illite
Harmony	10.1	59.0	30.9	25.4	Smectitic and some Illite
Portwing	30.9	44.4	24.7	10.1	Illitic with Smectite
1:2 Fargo: Serden Mix	71	16	13	8.0	Smectitic with some Illite
2:1 Fargo: Serden Mix	34	30	32	18	Smectitic with some Illite
Fargo	3	44	53	29	Smectitic with some Illite
Portwing	34	24	39	15	Illite and smectite

Appendix Table 2. Particle size distribution, CEC7[11] and mineralogy of soils used for prediction data from Chaudhari, (2001), Chiang et al., (1987) and Shainberg et al., (1981)

Soil	Paper	Sand (%)	Silt (%)	Clay (%)	CEC7 $\mathrm{cmole_c\ kg^{-1}}$	Mineralogy
Silt Loam	Chaudhari 2001	42.6	34	23.4	18.3	Mixed superactive
Clay Loam	Chaudhari 2001	40.5	23.8	35.7	36.5	Smectitic
Clay	Chaudhari 2001	23.5	21.2	55.3	55.2	Smectitic
Fallbrook	Shainberg et al., 1981	71	13	16	13	Mixed Superactive
Pachappa	Shainberg et al., 1981	69	20	11	9	Mixed Active
Gila	Shainberg et al., 1981	74	16	10	10	Mixed Superactive
Cecil	Chiang et al., 1987	78	11	11	3.7	Kaolinitic
Davidson	Chiang et al., 1987	41	22	36	11.2	Kaolinitic
Iredell	Chiang et al., 1987	64	20	16	15.4	Mixed Active

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[11] using Ammonium Acetate pH 7

Appendix Table 3. Soil clay mineralogy class, USDA particle size ranges, CEC_7, EC sat paste and SAR range of soil horizons used for the verification data.

Mineralogy	Number of Horizons	Sand range (%)	Silt range (%)	Clay Range (%)	CEC range ($cmol_c\ kg^{-1}$)	EC Range ($dS\ m^{-1}$)	SAR Range
Smectitic	217	0.73-71.3	12.6-80.2	8.9-69.2	7.2- 44.9	0.27-27.4	0-68
Mixed Superactive	350	1.1-94.9	2.8-84.2	2.3-64.3	4.1-39.3	0.5-21.2	0-441
Mixed Active	37	2-83.2	9.3-53.4	7.5-53.1	6.3-37.5	1-25.2	0-66
Mixed Semiactive	11	0.9-19.1	22.6-63.7	30.3-68.2	9.2-28.1	0.86-26.8	2-100

Appendix Table 4. GMRMSE of functions to predict K_{sat} on different soil mineralogy classes based of the NCSS natric great group dataset. 64 of the samples were Kaolinitic, 168 were mixed active, 30 were mixed super active and 472 were smectitic.

Equation	Kaolinitic (cm day^{-1})	Mixed Active (cm day^{-1})	Mixed superactive (cm day^{-1})	Smectitic (cm day^{-1})
McNeal 1968	2.4	1.69	5.16	4.27
Rosetta I	3.62	2.51	9.4	11.6
Rosetta II	2.36	1.67		14.5
Ahuja et al., 1984	2.4	3.98	22.2	35.2
Campbell, 1985	18.79	10.28	13.6	6.8
Campbell and Shiozawa, 1995	4.2	5.06	27.01	25.3
Cosby et al., 1984	38.3	9.6	8.4	161258
Puckett et al., 1984	20782	1925	344	1196
Dane and Puckett, 1994	123	18.45	9.15	15.23
Brakensiek et al., 1984	11.77	3.25	10.16	5.18
Saxon et al., 1986	42.6	18.3	14.6	10.4
Hypres (Wösten et al., 1999)	6.81	6.25	5.42	9.59
Minasny and McBratney, 2000	5.05	1.65	6.23	7.95
Tyler and Wheatcraft, 1989	1.99	2.39		26.28

Appendix Table 5. Pedotransfer functions generated in this report to predict K_{sat}. Literature data is from Shainberg et al., 1981, Chaudhari 2001 and Chiang et al., 1987

Function	GMRMSE	GMSE	R^2	GMRMSE	GMSE	R^2
	cm day^{-1}	cm day^{-1}		cm day^{-1}	cm day^{-1}	
	Klopp 2015 data			Literature data		
A. ln(Ksat)=3.81-0.045*clay	5.98	0.18	0.79	5.62	1.08	0.53
B. ln(Ksat)=7.6015.99*$w_{1/3}$	2.44	0.68	0.66	7.2	3.41	0.67
C. ln(Ksat)=4.1-0.08*$\frac{Clay*CEC}{Clay}$	4.15	0.27	0.68	4.1	0.61	0.65
D. ln(Ksat)=8.18-0.1*clay-0.099*CEC	5.35	0.33	0.33	8.5	8.5	0.58
E. ln(Ksat)=2.49-0.071*$\frac{Clay*CEC}{Clay}$+0.07*sand	4.08	0.82	0.78	9.3	4.2	0.50
F. ln(Ksat)=2.53-0.0005*$\frac{Clay*CEC}{Clay}$+0.28*EC-0.26*SAR	6.95	0.21	0.53	48	0.063	0.12
G. ln(Ksat)=10.5-0.051*(Clay*CEC)/Clay+0.09*sand-7.53*ρb	3.02	0.79	0.82	22	1.3	0.13
H. ln(Ksat)=2.09-0.0365*$\frac{Clay*CEC}{Clay}$ +0.057*sand+0.205*EC-0.16*SAR	3.14	0.61	0.7	5.4	0.64	0.51
I. ln(Ksat)=7.64-0.023*$\frac{Clay*CEC}{Clay}$+0.071*sand-5.22*ρb+0.197*EC-0.159*SAR	2.68	0.6	0.73	8.0	0.45	0.3
J.ln(Ksat)=9.5-0.059*(Clay*CEC)/Clay+0.067*sand-6.0*ρb	4.78	1.09	0.49			
K. ln(Ksat)=5.17-0.054*$\frac{Clay*CEC}{Clay}$ +0.052*sand-2.1*ρb+0.17*EC-0.0.093*SAR[1]	3.28	1.08	0.69			

[1] Uses a combination of data used for prediction and validation 75% of pooled data is used in prediction and 25% of the data is used in validation

Appendix Table 6. Predicted change in relative hydraulic conductivity (K_{rel}). The predicted K_{rel} uses the equation 15. The measured K_{sat} at high EC low SAR (meas K) is the highest EC and lowest SAR treatment that was measured on a given soil. GMRMSE and GMRE are in units of (cm day^{-1})

Function		R^2	GMRMSE	GMRE	R^2	GMRMSE	GMRE
		Klopp 2015 Validation			Literature Validation		
L.. ln(Krel)=0.023*EC-0.143*SAR	measK	0.58	1.93	0.97	0.74	4.34	0.99
	PredK	0.73	3.14	0.47	0.51	11.0	0.17
13. M.Ln(Krel)=0.000215*EC*clay-0.00341*SAR*clay	measK	0.63	1.85	1.0	0.83	3.45	0.75
	Pred K	0.73	3.28	0.49	0.57	8.71	0.27
N. Ln(Krel)=0.00098*EC*CEC-0.00533*SAR*CEC	measK	0.68	1.8	1.1	0.81	7.32	0.42
	Pred K	0.75	3.01	0.53	0.60	17.08	0.15
O. Ln(Krel)=0.00217*EC*CEC-0.001*EC*Clay-0.00473*SAR*CEC-0.00046*SAR*Clay	measK	0.66	1.81	1.05	0.81	6.76	0.99
	Pred K	0.74	3.14	0.51	0.59	16.0	0.16
Ln(Krel)=-0.65+0.0047*EC*CEC-0.00272*SAR*CEC[I]	measK				0.66	3.33	0.92
	PredK				0.50	9.0	0.21
P. ln(Krel)=0.0199*EC-0.0853*SAR[I]	measK				0.66	3.99	1.99
ln(KsathighEC)=5.01-0.0503*(Clay*CEC/Clay)+0.0568*Sand[I]	Pred Kr				0.64	7.87	0.91

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[1] Uses a combination of data used for prediction and validation 75% of pooled data is used in prediction and 25% of the data is used in validation

Appendix Table 7. Functions created to predict soil water retention curves using the van Genuchten function. w_r was assumed to be 0. Verification data sets 1 is samples not used in prediction equations from Klopp 2015 and Verification set 2 is Soil survey characterization data of soils that were classified as sodic. RMSE and Bias are in (g g^{-1}).

Equation	RMSE	Bias	R^2	RMSE	Bias	R^2
	Klopp 2015			Characterization data		
A1..w_s=0.41+0.0075*clay ln(α)=-2.91+0.0051*clay ln(N)=0.34-0.0041*clay	0.089	0.062	0.82	0.10	0.009	0.47
A2.. w_s=0.14+1.42*w1/3 ln(α)=-3.11+1.0*w1/3 ln(N)=0.29-0.253*w1/3	0.042	-0.034	0.91	0.059	-0.032	0.78
A3.ws=0.318+0.0023*clay+ 0.0118*CEC ln(α)=-3.65-0.0258*clay+0.077* CEC ln(N)=0.382-0.00247*clay +0.00405*CEC	0.0368	0.035	0.865	0.10	0.006	0.52
A4..ws=0.376+0.00129*(clay*CEC)/clay ln(α)=-4.28-0.064*(clay*CEC)/clay ln(N)=0.3222-0.0052*(clay*CEC)/clay	0.039	0.011	0.80	0.086	0.020	0.52
A5.w_s=0.27+1.26*w1/3 -0.00165*clay ln(α)=-3.05+1.09*w1/3-0.0247*clay ln(N)=0.29-0.25*w1/3 -4.1*10-8 clay	0.039	-0.025	0.86	0.058	-0.02	0.75
A6.. ws=0.672+0.141*(clay*CEC)/clay-0.0047*sand ln(α)=-2.05-0.064*(clay*CEC)/clay-0.042*sand ln(N)=0.3222-0.0052*(clay*CEC)/clay+0.0047sand	0.036	-0.002	0.86	0.10	0.015	0.36
A7. w_s=0.68-0.00074*clay+0.0042*CEC+0.004*sand ln(α)=1.88-0.072*clay-0.037*CEC-0.00648*sand ln(N)=0.084+0.0061*clay+0.0089*CEC+0.0036*sand	0.046	0.013	0.86	0.08	0.005	0.55
A8. w_s=0.325+0.0018*clay+0.011*CEC+0.0025*SAR ln(α)=-3.64-0.027*clay+0.076*CEC+0.0045*SAR ln(N)=0.38-0.0024*clay-0.00399*CEC-0.00025*SAR	0.058	0.026	0.865	0.11	0.025	0.51
A9. w_s=0.332+0.0017*clay+0.011*CEC+0.0025*SAR-0.002*EC ln(α)=-3.48-0.027*clay+0.076*CEC+0.005*SAR-0.049*EC ln(N)=0.38-0.0024*clay-0.00399*CEC-0.00026*SAR+0.00164*EC	0.058	0.026	0.865	0.107	0.023	0.54
A10.w_s=0.671-0.0011*clay+0.0043*CEC+-0.00396*sand-0.00239*EC+0.0024-0.002*SAR	0.051	0.023	0.868	0.09	0.017	0.56

ln(α)=-2.83-0.030*clay+0.057*CEC-0.024*EC-0.0042*SAR ln(N)=0.37-0.0023*clay-0.0039*CEC-+8.5*10^{-5} sand+0.00165*EC-0.00026*SAR						
A11. w_s=0.18+0.0025*(clay*CEC)/clay+9.7*10^{-5} *SAR/EC+0.90*$w_{1/3}$+0.52*w_{15} ln(α)=-3.9+0.083*clay*CEC/clay+0.02*SAR/EC-4.26*$w_{1/3}$+3.66*w_{15} ln(N)=0.347-0.00374*clay*CEC/clay-0.00056*SAR/EC+0.12* $w_{1/3}$ -0.56* w_{15}	0.032	-0.019	0.91	0.068	-0.002	0.76

Chapter 5 General Conclusions

Sodic soils have been characterized as those having an exchangeable sodium percentage (ESP) greater than 15 % and electrical conductivity (EC) less than 4 dS m^{-1} (Richards, 1954). For a soil to be classified within the natric[12] great group by the USDA Soil Taxonomy it also must have an argillic horizon (i.e., a subsurface horizon with a specified increased clay content with depth) and a prismatic or columnar soil structure. No soil physical property is currently used to classify soils as sodic. For determining whether irrigation waters are hazardous to soil physical properties several soil scientists have suggested threshold curves of EC versus sodium adsorption ratio (SAR[13]) to identify whether irrigation water has a high or low sodicity risk. These EC-SAR threshold curves were fashioned based upon a relative change in infiltration rate or saturated hydraulic conductivity compared to a solution of high EC and low SAR levels. When measuring the hydraulic conductivity of saturated soils of varying textures and clay mineralogy, soils dominated by smectite clays and with greater percentage of clay had larger decreases in soil saturated hydraulic conductivity when infiltrated with solutions of low EC and high SAR.

Smectite clays are the only soil clay type that undergoes changes in swelling in response to changes in EC and ESP. Smectite also has much greater plasticity than other soil clay types and the plasticity increases under high SAR and low EC. The osmotic effect from solution with high EC can prevent the interlayer of the smectite from expanding when the ESP is high.

Properties used to identify swelling hazard or plasticity of the soil could distinguish soils that contain appreciable smectite, from soils that contain little or no smectite. In particular, the liquid limit (LL) is much higher for sodium smectite compared to calcium smectite. Calcium

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[12] Sodic is a term used by the U.S. Salinity Laboratory and a large segment of the soil science community. Natric is is a taxonomic term for a subsurface diagnostic horizon. Natric horizons meets the same chemical criteria used by the Salinity Laboratory to identify a sodic soil.

[13] ESP is a soil property while SAR is a solution property but they can be used interchangeably because SAR can be used to predict ESP.

smectite has much higher liquid limit compared to clay grade mica (illite) and kaolinite. The liquid limit of kaolinite and mica clays does not change as ESP increases because they cannot free swell. Liquid limit is used in classification of soils for geological engineering with the USCS soil classification system to distinguish the effects of clay behavior on soil materials. Using a soil property related to clay behavior can identify soils that have clays that are smectitic and, therefore, able to free swell at high ESP levels and low EC levels.

The first objective of my thesis was to find a soil property sensitive to soil sodicity that can be measured rapidly; the property must be related to swelling clay behavior. The second objective was to determine the response of soil hydrologic properties to soil solution ESP and SAR. The third objective was to compare measured soil hydrologic properties to functions that are used to predict soil hydrologic properties and create a function that can predict the response of soil hydrologic properties to clay mineralogy and solution composition.

Chapter 1

The objectives of the first study which appears in Chapter 1 were to determine the change in soil Atterberg limits and soil coefficient of linear expansion (COLE) from EC and ESP. Three smectitic soils from South Dakota and were treated to salt concentrations between 5 and 40 meq l^{-1} with ESP values between 0 and 50. To create the high ESP low EC treatments soils were treated by applying a dry sodium carbonate to a calcium saturated soil. The higher salinity treatments were created using a mix of sodium and calcium chloride. Soil LL and COLE increased at high ESP and low EC levels. The change in soil LL and COLE was small at ESP levels between 0% and 15% but once ESP reached 25% the LL and COLE increased at 5meq L^{-1} salinity level. Salinity levels of 40 meq l^{-1} prevented the LL and COLE from increasing at ESP levels of 50%, a result of the osmotic effect.

There was an increase in swelling from high ESP and low salinity and a decrease in the swelling from increasing salinity levels as has been found on smectitic clays, but the magnitude was not the same. McNeal (1968) assumed the smectite in soils swelled as a Wyoming bentonite which was not supported by the results of this study. The dry sodium carbonate treatment was able to effectively increase soil ESP while maintaining low EC levels showing smectite clay presence and sensitivity to soil sodicity.

Chapter 2

Chapter 2 reports the results and a second study to further investigate the interaction of soil clay types, swelling related soil properties and ESP. Atterberg limits and COLE were measured on selected pure soil clays and silt mixed together along with on natural soils of a range of mineralogy. Water retention curves were measured on the natural soils, measuring water uptake by swelling clays. The synthetic soils covered a range of clay contents and select clay types.

The soil LL and COLE were dependent on the amount of bentonite or Fullers earth present in the sample with the bentonite have a much greater degree of free swelling compared to the Fuller’s earth. Synthetic soils containing kaolinite had a much lower COLE and LL swelling in both sodium or calcium saturated state. The smectitic soils increased in liquid limit, COLE and water retention at high ESP, whereas the soils that were not smectitic did not show increases in liquid limit or COLE

Measuring water retention at -102 or -336 cm or liquid limit in calcium saturated state and comparing to a high ESP state can identify soils that contain an active smectite clay fraction. Natural smectitic soils display a lower swelling response to ESP compared to the bentonite. Soils with smectite in their clay fraction can be identified by measuring -102 or -336 cm matric potential, liquid limit, or soil COLE without the need of semi-quantitative X-ray diffraction data by measuring in a 0% ESP state and a high ESP state made by a dry sodium carbonate treatment.

Chapter 3

Soil hydrology is important in water and salt transport in salt affected soils. High ESP and low EC decreases saturated hydraulic conductivity in certain soils in which most are smectitic. Water transport also is important in unsaturated conditions where soil water retention and unsaturated hydraulic conductivity becomes important. Determining what range of water potential on the water retention curves are affected by ESP is important in managing soil water and irrigation scheduling. Chapter 3 reports soil water retention curves measured on the three smectitic soils from South Dakota with salt concentrations between 5 and 40 meq l^{-1} and with ESP levels of 0 to 50. Water retention was measured on all 6 natural soils using the low salinity calcium saturated treatment and high ESP treatments created using sodium carbonate. Saturated hydraulic conductivity was also measured on all the natural soils. Water retention curves were fit with the van Genuchthen shape fitting function. Water retention increased from -15300 cm matric potential and greater (wilting point until saturation) from increasing ESP at low EC levels in the smectitic soils and there was no change in the kaolinitic soil. High EC reduced the effect of high ESP increasing water retention on the smectitic soils.

Chapter 3 also reports the results of a saturated hydraulic conductivity a study and found hydraulic conductivity decreased on all soils at high ESP and low EC. Natural smectitic soils had a larger decrease in saturated hydraulic conductivity and began to decrease at lower SAR levels compared to non-smectitic soils. The only van Genuchthen fitting parameters that changed was the saturated water content. The smectitic soils had the largest changes in soil hydrologic properties from high ESP whereas the non smectitic soils had a much smaller change in soil hydrologic properties from solution ESP.

Chapter 4

Measuring soil hydraulic properties is time consuming to do on soils of a range of texture and mineralogy, so correlating the changes in soil physical properties to properties available in basic soil surveys is useful for predicting soil hydrology on a landscape basis. Chapter 4 reports an evaluation of existing pedotransfer functions PTFs and new PTFs deigned to indicate the effect of clay mineralogy and solution composition on soil hydrologic properties. Two PTFs were previously developed to predict changes in soil saturated hydraulic conductivity under solution EC and ESP combinations.

The McNeal function is the most widely used hydraulic conductivity model and is used to simulate solution change in Hydrus 1-D. The McNeal function requires quantitative X-ray diffraction of soil smectite content and the assumption behind soil smectite behaving as Wyoming bentonite in the McNeal model was unfounded in chapter 2. Identification of soil smectite content is expensive and time consuming and is not readily available in most cases with soil characterization data. Many other PTFs have been created to predict soil saturated hydraulic conductivity and the soil water retention curve based primarily upon soil particle size analysis, organic matter content and dry bulk density. These functions do not account for soil clay type and the influence of solution EC and SAR on soil hydrology.

These previously developed PTFs and the McNeal function were analyzed using the measured soil hydrologic properties reported in chapter 3 and soil hydrologic properties from Klopp (2015). New functions were then created to predict the change in saturated hydraulic conductivity and water retention with solution EC and SAR. A PTF to predict relative saturated hydraulic conductivity changes with EC and SAR also was developed.

The previously developed PTFs to predict saturated hydraulic conductivity and water retention performed the worst on soils that were smectitic. The water retention PTFs from the literature performed worst in the wet range of the water retention curve above field capacity. The new PTFs introduced in Chapter 4 improved prediction of saturated hydraulic conductivity on soils by accounting for CEC, EC and SAR. The prediction of soil water retention curves also was improved including at greater than -336 cm matric potential. A PTF was created that could predict the relative saturated hydraulic conductivity relationship without the need for X-ray diffraction data with a similar root mean square error to the McNeal function. Including EC, SAR and CEC in functions improved function performance on the prediction of soil hydrologic properties.

Final Conclusions

Smectite clays are the main soil component that is affected by soil ESP and SAR. Smectitic soils show an increased liquid limit, COLE and water retention at potentials above -15300 cm H_2O from high ESP and low EC. Smectitic soils also had the largest decreases in saturated hydraulic conductivity from high ESP and low EC. Previously developed functions to predict soil hydrologic properties also performed the worst in smectitic soils. Soils with an active smectite content can be identified rapidly by measuring liquid limit or water retention when treated to a high ESP level and comparing to a calcium saturated state. Changes in soil hydrologic properties from soil solution composition can be predicted using soil CEC, clay content, EC and SAR without the need to measure soil smectite clay content using X-ray diffraction.