# BRINE-CONTAMINATED SOILS IN WESTERN NORTH DAKOTA:

# SITE ASSESSMENT METHODOLOGY AND A NEW IN-SITU REMEDIATION METHOD

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Aaron Wallace Klaustermeier

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**Title**

Brine-Contaminated Soils in Western North Dakota: Site Assessment Methodology and a New In-Situ Remediation Method

**By**
Aaron Wallace Klaustermeier

The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

**MASTER OF SCIENCE**

SUPERVISORY COMMITTEE:

Aaron Daigh
Chair

Thomas DeSutter

Abbey Wick

Ryan Limb

Approved:

April 5, 2016
Date

Francis Casey
Department Chair

# ABSTRACT

Anthropogenic soil salinity caused by produced water (i.e., brine) contamination is an issue in all oil and gas producing regions. The objectives of this research are to develop soil electrical conductivity (EC) conversion equations for rapid site assessment of brine spills and to determine the efficacy of crystallization inhibitors as an in-situ remediation method. Conversion equations were developed for soil-to-water suspensions and saturated paste extracts ($EC_e$) on brine-contaminated soils. These new equations provided the best prediction of $EC_e$ when compared to 14 other equations reported in the literature. A crystallization inhibitor ($C_{18}Fe_7N_{18}$) applied to NaCl-contaminated soils using various concentrations and methods of application yielded dendritic salt crystals above the soil surface. On average, between 0.29 and 0.57 g $g^{-1}$ of NaCl salts effloresced when surface applying a 0.01M concentration of the crystallization inhibitor. Results from these studies will guide consultants and researchers in the assessment and remediation of brine-contaminated soils.

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# DEDICATION

I would like to dedicate this thesis to my grandparents, Harlen and Darlene Milbradt.

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# GENERAL INTRODUCTION

Soil salinization is a major problem worldwide, affecting range and farmlands in more than 100 countries, including the United States (Squires and Glenn, 2009; Szabolcs, 1989). Over the last two decades, oil and gas operators have considerably increased the amounts of oil and gas exploration in the Bakken and Three Forks Formations within the Williston Basin of western North Dakota due to advancements in horizontal drilling and hydraulic fracturing technologies. This increase in oil and gas production also innately results in a substantial rise in anthropogenic salinity caused by produced water (i.e., brine) spills and pipeline leaks.

Brine is considered a regulated byproduct of the oil and gas industry (Guerra et al., 2011; Clark and Veil, 2009; Fakhru'l-Razi et al., 2009; Herkelrath et al., 2007) and is composed mainly of formation and injection waters, dissolved oil and soluble salts (Fakhru'l-Razi et al., 2009; Whittemore, 1995). Oil and gas wells throughout the Bakken formation and Williston basin produce large quantities of brine with salt concentrations four to ten times greater than ocean water (Murphy et al., 1988). Electrical conductivities (EC) and total dissolved solids (TDS) of these brines often exceed 200 dS $m^{-1}$ and 100,000 mg $L^{-1}$, respectively (Dresel and Rose, 2010; Sublette et al., 2007; Aschenbach and Kindscher, 2006; Otton, 2006; Sublette et al., 2005; Keiffer and Ungar 2002; Atalay et al., 1999; Jacobs et al., 1992; Munn and Stewart, 1989; Murphy, 1988; McFarland et al., 1987; Pitre, 1984; Jury and Weeks, 1978; Latta, 1963). Accidental or deliberate discharges of brine into the environment result in high soil salinity levels which leads to overall land degradation and reductions in plant productivity (Barzegar et al., 1997, Murphy et al., 1988).

Previous literature reports soil EC conversion equations for determining the extent of salinity and sodicity on agricultural and rangelands. However, only a small portion of those studies developed equations specifically for salinity resulting from brine contamination (Zhang et al., 2005; Pittman et al., 2001). The extent and rapidness of remediation depends on the assessment tools used to quantify the soil salinity. Therefore, these assessment tools (i.e. soil-test methods) must be precise and done in a timely manner to ensure remediation success. Converting measurements obtained from soil-to-water suspensions to predictions of a saturated paste extract EC (referred to as $EC_e$ hereafter) is effective in reducing the time and resources involved in determining the extent of salinity on brine-impacted land. Unfortunately, the literature lacks conversion equations developed and validated for the range of $EC_e$ values observed on brine spill sites (Zhang et al., 2005; Chi and Wang, 2010).

Many studies also assess the efficacy of various ex-situ and in-situ remediation practices for brine-contaminated soils (Harris et al., 2005; Sublette et al., 2005; Ashworth et al., 1999; Atalay et al., 1999; Halvorson and Lang, 1989; Auchmoody and Walters, 1988; Jury and Weeks, 1978). These in-situ and ex-situ remediation methods reduce salt concentrations and allow vegetative re-growth of the area. However, the resources and/or the rate of water flow through brine-affected soils make these current remediation methods time-intensive, invasive, costly, and limited for long-term success (Thimm, 1990; Hayashi et al., 1998). An ideal remediation technique would involve maintaining soil integrity while permanently removing salts from the brine-affected site.

Crystallization inhibitors are used in previous studies to reduce building and monument decay from salts (Gupta et al., 2012; Rivas et al., 2010; Lubelli and van Hees, 2007; Rodriguez-Navarro et al., 2002; Selwitz and Doehne, 2002) and have the potential to be used as a remediation method on brine-contaminated soils. The application of crystallization inhibitors to soil is a more permanent and less invasive remediation tactic when compared other common forms of remediation (chemical amendments and leaching; topsoil excavation). Instead of displacing salts downward temporarily, the use of a crystallization inhibitor would work with the natural processes of soil water evaporation to transport salts upward and effloresce on the surface. Additionally, this upward crystallization would allow salts to be permanently extracted from the soil surface without destroying thousands of years of pedologic soil development, as seen with topsoil excavation.

The objectives of this thesis are to 1) develop soil EC conversion equations for soils contaminated with NaCl salts as a tool for rapid site assessment and 2) assess the efficacy of a surface applied crystallization inhibitor application as a new, rapid remediation method. To meet these objectives, field and laboratory studies were conducted to characterize a range of brine spills (i.e., recent and past brine spills) in North Dakota, use these brine spill sites to accomplish objective 1, and develop and optimize the concept of using crystallization inhibitors to harvest brine salts from the soil surface. These studies will add to the current knowledge of brine spill site assessment and effective remediation strategies.

# LITERATURE REVIEW

## Williston Basin

The Bakken formation is located within the subsurface of the Williston basin and covers approximately 52 million hectares of western North Dakota, Montana, Saskatchewan and Manitoba (LeFever, 1991; Gerhard et al., 1982; Meissner, 1978; Nordquist, 1953). The Bakken lies roughly 3000 meters deep between the Lodge Pole and Three Forks formations and largely consists of organic shales that are known to contain large amounts of petroleum found in fractured reservoirs above and below the unit (Meissner, 1978; Dow, 1974; Williams, 1974). These formations potentially contain the largest amounts of recoverable oil in the United States (7.38 billion barrels), with current production in the region ranking second only to Texas (US EIA, 2015). Recent advancements in drilling technologies such as horizontal drilling and hydraulic fracturing have made this amount of oil production and extraction economically viable in the region.

## Oil and Gas Production in North Dakota

### *Oil and Gas Production History*

North Dakota has undergone a series of three major oil and gas exploration events over the last century (LeFever, 1991). North Dakota’s first oil boom occurred during the 1950’s and proceeded slowly due to geologic and technological limitations. Initially, engineers did not consider the Bakken formation for oil and gas development due to its deep, impermeable shale layers and naturally fractured reservoirs (LeFever, 1991). Regardless of these restrictions, exploration and drilling continued to rise during the 1960’s and 70’s as oil companies found other large oil fields. Conventional (vertical) drilling was the main method of oil and gas extraction during these periods. Horizontal drilling first occurred during the second North

Dakota oil boom in 1987, and by 1989, 45% of the oil produced from the Bakken originated from horizontal wells (LeFever, 1991). Production rates remained steady until the early 2000's, when new methods advanced in horizontal drilling and hydraulic fracturing.

## Hydraulic Fracturing/Horizontal Drilling

Hydraulic Fracturing (i.e., Fracking) is a process used during unconventional oil well development to increase formation permeability and oil and gas extraction (Clark, 1949). The fracking process involves the injection of a granular, viscous fluid under high pressures to cause fracturing within the formation and the subsequent movement of oil and gas through fracture openings (Hubbert, 1972; Reynolds et al., 1954; Scott et al., 1953; Clark, 1949). The granular material (mainly sand) props up the fissures created during the fracturing process (Clark, 1949). Fracking is necessary in this region of the U.S. to increase reservoir conductivity and extract economical quantities of oil and gas due to the accumulation of oil in tight, sedimentary shale formations (Guerra et al., 2011). Horizontal drilling in conjunction with fracking techniques increases extraction efficiency and optimizes land use, allowing producers to extract oil laterally from an area with a minimal number of wells.

## Current and Future Oil Production in North Dakota

Current exploration efforts within the Bakken utilize hydraulic fracturing and horizontal drilling techniques in lieu of conventional vertical methods, allowing greater amounts of oil and gas produced than in previous decades. As a result, daily oil production within the Bakken has increased approximately 1,000-fold since the early 2000's due to these new drilling methods (ND DMR, 2015). As of October 2015, > 10,000 wells within the Bakken produce > 100 barrels per day, (i.e., > one million barrels of oil per day; ND DMR, 2015). Further use of these technologies coupled with the amount of recoverable oil reserves will allow North Dakota to continue being a leading oil producing state for decades to come. However, the amount of produced water (i.e., brine) and its spillage has increased along with the increase in oil and gas production. Historical statistics on the occurrence and amount of land contaminated by brine went largely un-documented until 2001 when the North Dakota Industrial Commission (NDIC) began implementing detailed spill reports. Since then, over 78 million liters of brine are documented to have been spilled on and off well pads throughout western North Dakota as of December 23rd, 2015 (Figure 1; ND DOH, 2015). However, many believe these volumes to be conservative estimates due to the suspected underestimation of spill volumes and illegal dumping of produced waters

## Oil and Gas Produced Waters (i.e., Brine)

### *Origin and Chemical Makeup*

Oil and gas wells throughout the Bakken formation yield large quantities of produced water (i.e., brine) with salt concentrations up to ten times more saline than ocean water (USGS DOI, 2013; Murphy et al., 1988). Brine is considered a regulated waste byproduct of the oil and gas industry (Guerra et al., 2011; Clark and Veil, 2009; Fakhru'l-Razi et al., 2009; Herkelrath et al., 2007) and is composed primarily of formation and injection waters, dissolved oil and salts (Fakhru'l-Razi et al., 2009; Whittemore, 1995). Dissolved salts in the brine (mainly NaCl; 90%) originate from halite deposits formed within the oil and gas-enriched shale formations (McMillion, 1965; Anderson and Hansen, 1957). The salt contents in these brines throughout the U.S., including North Dakota, exceed electrical conductivities (EC) of 200 dS $m^{-1}$ and total dissolved solids (TDS) concentrations of 100,000 mg $L^{-1}$ (Daigh and Klaustermeier, 2016; Dresel

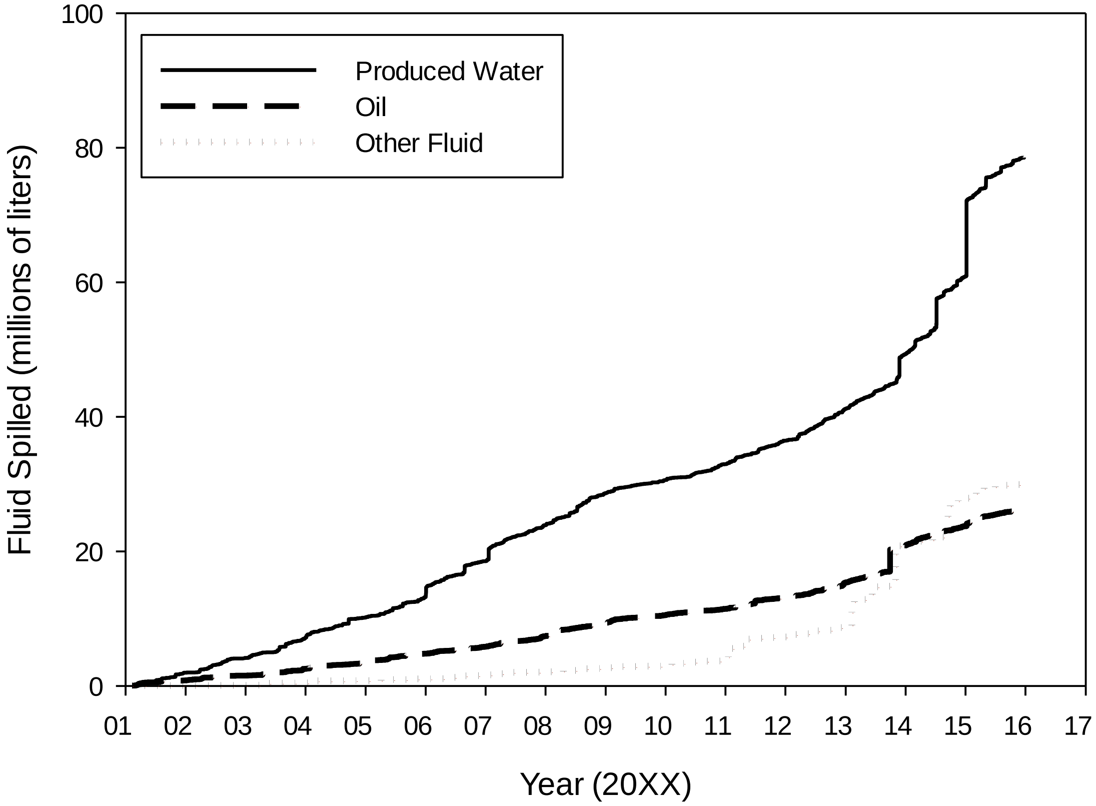

**Figure 1.** Quantity of fluid spilled on and off oil drill pads during and after oil and gas exploration efforts in North Dakota from February 9th 2001 through December 23rd 2015 summarized from the North Dakota Department of Health spill database (ND DOH, 2015). The first date coincides with when the North Dakota spill records began reporting the amount of fluid spilled.

and Rose, 2010; Sublette et al., 2007; Aschenbach and Kindscher, 2006; Otton, 2006; Sublette et al., 2005; Keiffer and Ungar 2002; Atalay et al., 1999; Jacobs et al., 1992; Munn and Stewart, 1989; Murphy, 1988; McFarland et al., 1987; Pitre, 1984; Jury and Weeks, 1978; Latta, 1963). However, the quantity and chemical composition of production brines depend on location and geologic formation (Murphy et al., 1988). In addition, as oil wells age they undergo a decline in oil extraction rates and an increase in brine production (Dal Ferro and Smith, 2007; Veil et al., 2004; Khatib and Verbeek, 2002), with some wells producing upwards of 100 barrels of brine for every barrel of oil (OTA 1984; U.S. EPA, 1977). In 2007, North Dakota wells produced an average of 3 and 18 barrels of brine for each barrel of oil and 28,000 $m^3$ of gas, respectively (Clark and Veil, 2009).

### *Past and Present Brine Disposal*

Once brine has been extracted along with oil and gas it must be transported and disposed of properly to ensure environmental protection. The NDIC and the North Dakota Department of Health (ND DOH) regulate produced water transport and its disposal in North Dakota, although regulations and methods of transport and disposal have changed over time. During previous oil exploration efforts in North Dakota, brines were disposed of in lined and oftentimes unlined evaporation pits or holding ponds (Gleason et al., 2014; Arocena and Rutherford, 2005; Kharaka and Dorsey, 2005; Patrick et al., 1987; U.S. EPA, 1977; Scalf et al., 1973; Fuhriman and Barton, 1971; Sackett and Bowman, 1905). These containment pits held wastewater until the evaporation of water and solidification of residues occurred for further disposal. This method allowed for mobile chloride salts found within the brine to leach deep into the soil profile and for the eventual decline in surface and groundwater quality due to excess salt contamination (Gleason et al., 2014; Murphy et al., 1988; Pettyjohn, 1973; Boster, 1967; Shaw, 1966; Krieger and Hendrickson, 1960). Saline leachate plumes generated from brine infiltration in the pits can exceed a 150 m radius and a 20 m depth due to persisting salt migration (Murphy et al., 1988). New oil and gas legislation was enacted in North Dakota in September, 2000 in an effort to end contamination from the use of these early methods (NDAC). Previous brine contamination resulted mainly from primitive storage and disposal practices, although recent changes in storage and disposal have still allowed large quantities of brine to contaminate important land and water resources.

Current brine disposal practices involve the use of tanker trucks, tank batteries and underground pipelines, and deep re-injection wells (Gleason et al., 2014; Guerra et al., 2011; Clark and Veil, 2009; Sublette et al., 2007; Harris et al., 2005; Vavrek et al., 2004; Patrick et al., 1987). Brine is extracted from a well along with oil and natural gas and must first be processed using a heater/treater device that removes the gas and heats up the water/oil mixture to induce separation (U.S. EPA, 1999). Once brine is separated from the oil and natural gas it is transported via underground pipeline to large tank batteries for containment and tanker truck transport before re-injection occurs. As of 2007, approximately 98% of produced water is injected in underground formations (Clark and Veil, 2009). Re-injection occurs in previously drilled, unproductive oil and gas wells or in wells drilled for the specific purpose of brine disposal (i.e., 40%; Clark and Veil, 2009). Produced wastewater can also be recycled for re-injection into oil-producing formations when using the hydraulic fracturing method (i.e., 59%; Clark and Veil, 2009; Patrick et al., 1987) or irregularly through treatment for livestock or irrigation water requirements (Fakhru'l-Razi et al., 2009; Veil et al., 2004). Although the efficacy of these current methods is documented, leakage and spillage are common events before re-injection and disposal occur and are increasing exponentially with the rise in oil and gas production.

### ***Brine Contamination***

The introduction of brine onto land surfaces historically originates from a multitude of sources, including but not limited to evaporation pits, container and pipeline overflow and leaks, operator error, and illegal dumping (ND DOH, 2015; Sublette et al., 2007). During previous oil and gas explorations, operators used evaporation pits to store and concentrate produced brines. Many evaporation pits have not undergone remediation and therefore still contain large quantities of salts. Convective and diffusive transport of these salts dissolved in soil water may result in ions migrating to adjacent soils not previously affected by brine. Contemporary storage and transport of brines include tank batteries and pipelines. These structures corrode and leak if not maintained properly and are vulnerable to damage by lightning strikes. Older tank batteries may exhibit visible signs of wear due to repeated expansion and contraction forces creating points of weakness on connecting parts. If these issues persist over time, leaks will occur. In addition, tank battery overflow is another common means of brine contamination. Overflow occurs when pressures become too high for connecting parts or when the amount of brine exceeds storage tank capacity. In Oklahoma, tank overflows accounted for 50% of brine spill incidents (Sublette et al., 2007). Typically, a well pad will contain multiple oil and brine tank batteries, which oil field operators periodically empty and/or inspect to prevent such leaks and spills from occurring. Since 2001, there have been over six thousand produced water spills throughout western North Dakota (Daigh and Klaustermeier, 2016; ND DOH, 2015).

### *Effects on Soil and Vegetative Health*

Brine contamination negatively effects the chemical and physical properties of soil. Brine-affected soils become saline-sodic because of the excess amounts of soluble salts, including mainly sodium ($Na^+$) and Chloride ($Cl^-$). Unlike other soluble salts, excess $Na^+$ negatively affects soil structure and reduces soil permeability and hydraulic conductivity (Yang and Barbour, 1992; Benson and Daniel, 1990; Mitchell et al., 1965). The infiltration of brine into soil skews the ratio of divalent to monovalent cations on soil exchange sites, affecting soil aggregation and flocculation. As a result, the $Na^+$ affected soil clay particles disperse and the soil loses structure (Atalay et al., 1999; Sandoval and Gould, 1978; Sherard et al., 1976). This degradation of soil structure and subsequent loss of vegetation and root structures leaves soils prone to a reduction in water infiltration and drainage capability as well as increased wind and water erosion and compaction (Norton and Strom, 2012; Newell and Connor, 2006; Barzegar et al., 1997). Only salt tolerant and adaptable plants can survive in some brine-contaminated soils (Gupta and Huang, 2014; Aschenbach and Kindscher, 2006; Vavrek et al., 2004; Keiffer and Ungar, 2002; Qadir et al., 1996; McFarland et al., 1987).

The salt content of brines affects plant water availability, water uptake, and nutrient absorption due to osmotic and ionic changes (Manousaki and Kalogerakis, 2011; Gawel, 2006; Huang and Redmann, 1995). Excess salts compromise osmotic regulation within plants. The salts reduce the soil osmotic water potential below the plant's osmotic water potential, causing plants to exert more energy to absorb water and prevent wilting. This osmotic pressure imbalance produces a physiological drought within the plant, greatly restricting plant water uptake even when ample amounts of soil water are present. Additionally, plant uptake of excessive quantities of ions (e.g., $Na^+$) may limit the uptake of other essential nutrients, inducing ionic stress in plants (James et al., 2011; Rahnama et al., 2010). The abundance of $Na^+$ in plant tissue leads to ion toxicity and creates nutrient imbalances within the plant, affecting the plants metabolism and basic functions (Gupta and Huang, 2014; Aschenbach and Kindscher, 2006; Wyn Jones, 1981).

## Conversion Equations for Site Assessment

To remediate brine-affected soils effectively, operators need accurate and timely soil analyses. Determining the extent of salinity using various soil-to-water suspension ratios is a more time and cost effective method compared to using the standard saturated paste extracts (Franzen, 2013). Furthermore, many scientists and environmental consultants determine EC in the field using portable conductivity meters. Most of these meters are limited in their EC measurement range (e.g., 0.1 – 20 dS $m^{-1}$), although brine often exceeds 200 dS $m^{-1}$ (Keiffer and Ungar, 2002). Using a soil-to-water suspension to dilute the salt concentration of a soil sample and then the use of an EC conversion equation is a timelier option for determining soil EC in these situations. Using optimal equilibration times, soil-to-water suspension EC can be calculated within a matter of minutes. These EC methods are found to be reliable for a wide range of soil textures and EC values (Khorsandi and Yazdi, 2011; Chi and Wang, 2010; Ozcan et al., 2006; Zhang et al., 2005; Hogg and Henry, 1984). Remediation strategies for brine spills rely on having accurate, reliable, and timely data so that the spill area is delineated and contained, and so first-response remediation actions can be made. Currently, most assessment strategies involve using saturated paste extracts ($EC_e$), and can take over 48 hr to get results. Using soil-to-water suspensions with shorter equilibration and preparation times will reduce the work and time involved in obtaining soil EC measurements.

Many studies have observed good relationships between 1:1 and 1:5 soil-to-water ratios ($EC_{1:1}$ and $EC_{1:5}$), and saturated paste extracts ($EC_e$). One study successfully developed conversion equations for soils with $EC_e$ ranging from 1 to 227 dS $m^{-1}$ for sodium ($Na^+$) based soils (Chi and Wang, 2010). However, their equations do not address an apparent heteroscedasticity as observed in another conversion equation study done by He et al. (2012). Another study observed a good relationship ($r^2 = 0.98$) between $EC_{1:1}$ and $EC_e$ for medium textured soils with an $EC_e$ ranging from 0.2 to 42.1 dS $m^{-1}$ (Hogg and Henry, 1984). In addition, Sonmez et al. (2008) developed equations for converting $EC_{1:1}$ and $EC_{1:5}$ to $EC_e$ using a loamy, NaCl, KCl and $CaCl_2$ based soil with soil $EC_e$ values ranging from 0.2 to 17.7 dS $m^{-1}$. However, conductivity factors are specific to ion species and associations and therefore these conversion equations are not as reliable in soils of different solution chemistries (Tolgyessy, 1993). Ion pairing of calcium and magnesium can result in different conductivity factors in comparison to that of NaCl. In a study conducted by Alzubaidi and Webster (1983), 50% of tested calcium and magnesium ions existed as ion pairs, whereas only 0.58-5.2% of sodium was paired with other ions.

## Current Remediation Methods

### *Topsoil Excavation*

Once a brine-affected soil is assessed for salinity levels and the spill area delineated, operators select a remediation option for the site of concern. Topsoil excavation and disposal are ex-situ remediation methods performed in situations where brine contamination is concentrated within a small area or when waterways or ground waters are in immediate danger of being polluted (Harris et al., 2005). Operators remove the contaminated soil with heavy equipment and machinery to the affected depth, which depends on the spill's areal extent, soil infiltration rate and time since the spill. After excavating a brine-contaminated soil, state permits are required to discard the contaminated soil at a disposal facility (ND DOH, 2015). The efficacy and rapidness of this method in reducing contamination are the main benefits for its application. However, this remediation option is invasive, costly and typically limited to small spill sites.

### *Addition of Chemical/Organic Amendments, Leaching and Subsurface Drainage*

Applying chemical amendments and leaching are common in-situ approaches to remediating brine spills. The physical roles of chemical amendments are to dilute salts, promote aggregation, reduce dispersion and increase water infiltration (Armstrong et al., 2015; Chaganti and Crohn, 2015; Murtaza et al., 2015; Ballasteros et al., 2014; Emami et al., 2014; Choudhary et al., 2011; Elrashidi et al., 2010; Wong et al., 2009; Tejada et al., 2006; Ilyas et al., 1997).

Calcium (particularly gypsum) amendments can be applied in-situ to replace sodium ions on contaminated soil exchange sites. This ion exchange allows the sodium to leach with water (precipitation or irrigation) through the soil profile, below where plants germinate (Amezketa, 2005; Harris et al., 2005; Knox and Sabatini, 2000; Ashworth et al., 1999; Atalay et al., 1999; Jury and Weeks, 1978). The amount of gypsum required to properly exchange with sodium varies depending on soil type (texture, structure), cation exchange capacity, exchangeable sodium percentage, drainage class and precipitation (Bahceci, 2008; Jury and Weeks, 1978). Furthermore, soil texture is an important aspect to consider in terms of a soil's leaching potential, as coarser textures will produce larger quantities of leachate through a soil profile. For fine textured soils, up to 30 pore volumes (i.e., 30 times of thoroughly saturating and draining the soil pore space) of leachate may be needed to replace $Na^+$ with $Ca^+$ when using gypsum (Jury and Weeks, 1978). Tile drainage is oftentimes used to intercept this leachate and remove the brine salts (Sublette et al., 2007; Jury and Weeks, 1978). The intercepted solutions are collected and properly disposed of to prevent further damage to land and water resources.

Organic materials are oftentimes used in conjunction with chemical amendments to amend the effects of excess salinity from brine contamination and can include straw, hay, mulch, sawdust, bark, woodchips, biosolids and biochar (Harris et al., 2005; Conway, 2001; Anderson, 2000; Dubey and Mondal, 1993; Sandoval and Gould, 1978). Applying a layer of organic materials over brine-contaminated soil reduces evaporation and salt transport to the surface. In addition, organic materials that are mixed into the soil break down, providing soil organic matter. Harris et al. (2005) successfully remediated a brine-impacted soil using hay without the addition of chemical amendments. Their observations suggest that tilling hay into brine-contaminated soil can reduce salinity and sodicity to the same levels as using gypsum or other chemical amendments, with the added benefit of introducing organic matter and rebuilding soil structure (Harris et al., 2005).

The use of chemical amendments, organic materials, leaching and drainage are expensive remediation methods due to their manufacturing, transportation and application costs. Additionally, the use of chemical amendments is effective only to the depth at which they are applied (Sublette et al., 2007; Robbins, 1986) and intense amounts of water and time (1 to > 1000 years) are required for their application to be effective (Jury and Weeks, 1978; See Appendix A for a preliminary estimate using the HYDRUS-1D code). Furthermore, the use of chemical and organic amendments and leaching on brine-contaminated soils may have limited long-term success due to the possibility of eventual re-salinization from deeper soil depths due to capillary water movement and salt migration (Hayashi et al., 1998; Murphy et al., 1988). Although the success of these current remediation techniques is apparent, an ideal remediation method would involve maintaining soil integrity while permanently removing salts from the affected site in a more efficient and economical manner.

## Crystallization Inhibitors and their Remediation Potential

A new in-situ remediation method proposed and evaluated in this thesis involves the application of a crystallization inhibitor to the soil surface and subsequent harvesting of crystallized salt efflorescence. Other researchers evaluated crystallization inhibitors on various types of porous stone to determine their ability to reduce damage and subsequently preserve important landmarks around the world. Salt crystals within a porous media begin to grow as evaporation occurs and exert pressure within the stone on pore walls, which can lead to damage over time. Crystallization inhibitors are chemical compounds used to prevent salt crystal formation and change salt crystallization growth habits (Bode et al., 2012). Other studies tested sodium and potassium hexacyanoferrate ($Na_4[Fe(CN)_6]$; $K_4[Fe(CN)_6]$) as crystallization inhibitors on various types of NaCl-contaminated stone. After the inhibitor applications, NaCl crystals grew upwards on the stone surface rather than internally, producing raised crystallized salt structures; more commonly called efflorescence (Gupta et al., 2012; Rivas et al., 2010; Lubelli and van Hees, 2007; Rodriguez-Navarro et al., 2002; Selwitz and Doehne, 2002). In a study conducted by Gupta et al. (2012), approximately 0.36 g $g^{-1}$ of applied NaCl salt in a fired clay brick and 0.47 g $g^{-1}$ of NaCl salt in a limestone sample effloresced on the object's outer surfaces when saturated with a 3 M NaCl salt solution and 0.001 M solution of potassium hexacyanoferrate. When the crystallization inhibitor concentration used increased by one magnitude, approximately 0.69 g $g^{-1}$ of the salt in the fired clay brick and 0.51 g $g^{-1}$ of the salt in the limestone effloresced on outer surfaces when saturated with the same 3 M salt solution (Gupta et al., 2012).

The crystallization inhibitor used in this study is ferric hexacyanoferrate ($C_{18}F_7N_{18}$; Figure 2); commonly known as Prussian blue. Prussian blue is a chemical compound that has historically been used as a color pigment for industry and artists (FDA, 2011), although it has also been used in the medical industry to aid in the reduction and excretion of radioactive materials, poisons and heavy metals in the body (Baldwin and Marshall, 1999; Pearce, 1994; Mulkey and Oehme, 1993). Prussian blue was chosen as the crystallization inhibitor for this study due to its stability and chemical inertness (Meussen et al., 1992; Sharpe, 1976). Other crystallization inhibitor compounds with similar chemical properties (i.e., sodium and potassium hexacyanoferrate) may have similar success rates when used to alleviate soil salinity. Crystallization inhibitor compounds range in price depending on quantity and demand. Chemical grade ferric hexacyanoferrate (VWR—Alfa Aesar, Ward Hill Massachusetts, USA) was

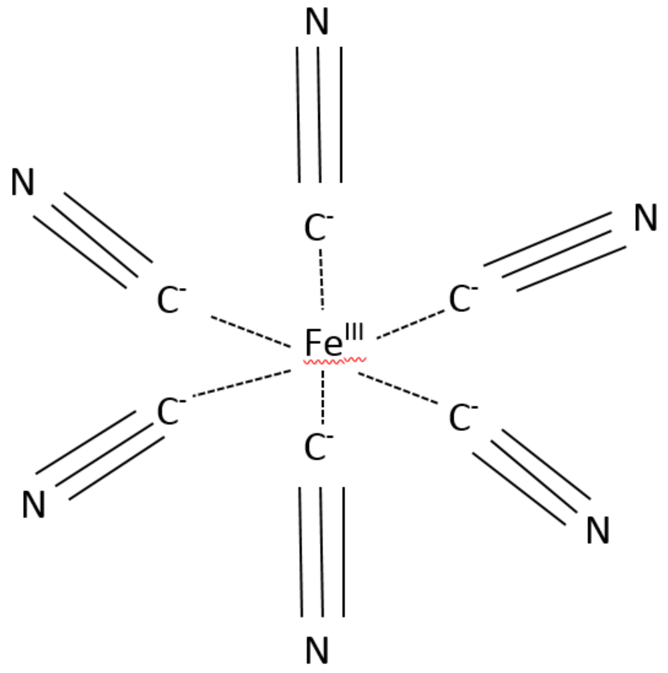

**Figure 2.** 2-D chemical structure of a hexacyanoferrate ($[Fe(CN)_6]^{3-}$) crystallization inhibitor compound.

purchased at a rate of $146/100 g for use in our chapter II study. However, the price of crystallization inhibitors varies depending on quantity purchased and is subject to change based on market demand. In ongoing field experiments, ferric hexacyanoferrate is being purchased at a rate of \$46 $kg^{-1}$ for an order of 140 kg.

Crystallization inhibitors could potentially allow for harvesting salts from the soil surface of brine-affected soils since these soils are a soft porous media similar to ridged porous media (i.e. stones and bricks). The use of crystallization inhibitors to remediate NaCl-affected soils is not assessed in any previous studies reported in the scientific literature. All current remediation methods involve the downward movement and extraction of salts. Harvesting salts from the soil surface would be a more permanent solution in reducing salinity on brine-affected sites. Rather than displacing salts downward temporarily, the use of a crystallization inhibitor would work with the natural processes of soil water evaporation to transport salts upward and effloresce on the surface. Furthermore, the use of crystallization inhibitors as an in-situ remediation method on brine-impacted soils could significantly reduce the time and resources associated with other physical or chemical remediation amendments due to an expedited remediation timeline.

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# COMPARISON OF SOIL-TO-WATER SUSPENSION RATIOS FOR DETERMINING ELECTRICAL CONDUCTIVITY OF OIL-PRODUCTION WATER CONTAMINATED SOILS[1]

## Abstract

Soil salinity caused by oil-produced water (i.e., brine) contamination is a major issue in regions of oil and gas development. However, rapid site assessment tools such as soil-to-water suspension electrical conductivity (EC) methods and conversion equations have not been previously calibrated and validated for brine-contaminated soils. Our objective was to compare three soil EC methods and derive conversion equations for EC values commonly observed at brine spill sites. Brine-contaminated soils from western North Dakota were assessed for salinity. Electrical conductivity was determined using 1:1 and 1:5 soil-to-water suspensions ($EC_{1:1}$, $EC_{1:5}$) and saturated paste extracts ($EC_e$). Soil EC equilibration times for soil-to-water suspensions were also assessed. Significant relationships ($r^2 = 0.91$ to $0.97$, $P < 0.0001$) existed among all methods for EC values ranging between 0 and 126 dS $m^{-1}$. Conversion equations were developed based on these relationships and then validated with an independent data set. These new equations reduced $EC_e$ prediction errors by 2 to 4.5 times when compared to 14 predictive equations reported in the

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[1] The material in this chapter was co-authored by Aaron Klaustermeier, Hannah Tomlinson, Aaron Daigh, Ryan Limb, Thomas DeSutter and Kevin Sedivec. Aaron Klaustermeier had primary responsibility for collecting samples in the field and for analyzing samples in the lab. Aaron Klaustermeier was the primary developer of the conclusions that are advanced here. Aaron Klaustermeier also drafted and revised all versions of this chapter. Aaron Daigh served as proofreader and checked the math in the statistical analysis conducted by Aaron Klaustermeier. This manuscript was submitted to the Canadian Journal of Soil Science.

literature. The conversion equations developed here are recommended for use in remediation efforts when converting $EC_{1:1}$ and $EC_{1:5}$ data to $EC_e$ on brine-contaminated and non-contaminated soils where $EC_e$ is highly correlated to Na concentrations.

## Introduction

Anthropogenic salinization due to oil-produced water (i.e., brine) spills are commonly experienced in areas of oil and gas development (Keiffer and Ungar, 2002). Brine spill first responders and researchers often require rapid site assessment tools in the field, although common soil electrical conductivity (EC) meters operate below the higher EC values of brine-contaminated soils. Soil-to-water suspension methods and their conversion equations to the preferred saturated paste extract EC ($EC_e$) are simple and effective tools that save time and effort during brine spill reclamation and research efforts. However, no calibration or validation of soil-to-water suspension methods and their conversion equations for brine-contaminated soils are reported in the scientific literature.

Soil contamination from oil and geothermal production brines, with similar solution chemistries as those in North Dakota, have been reported in Kansas (Latta, 1963), Ohio (Munn and Stewart, 1989), Oklahoma (Atalay et al., 1999; Sublette et al., 2005; Sublette et al., 2007), Pennsylvania (Dresel and Rose, 2010), Texas (McFarland et al., 1987), and California (Jury and Weeks, 1978). Oil and geothermal production brine is a concentrated mixture of dissolved salts; the most abundant being sodium chloride (NaCl) (Aschenbach and Kindscher, 2006). These brines can have an EC up to four to ten times greater than those observed in seawater (e.g., 200 dS $m^{-1}$) (Jury and Weeks, 1978; Keiffer and Ungar, 2002). As of December 23rd, 2015, approximately 78 million liters of brine have been spilled on and off drill pads during the oil and gas exploration in western North Dakota since Feb. 9th, 2001 (Figure 3; data summarized from the North Dakota Department of Health spill database). During this time, 6,247 brine spills have been reported to the North Dakota Department of Health and the North Dakota Industrial Commission (ND DOH, 2015). Once brine has been released onto the soil surface, the soil becomes sterile and void of vegetation, which can persist for decades until the salts are reduced or removed (Murphy et al.,1988). Since the early 2000s, these spills have resulted in thousands of brine spill reclamation efforts that require effective and rapid site characterization tools.

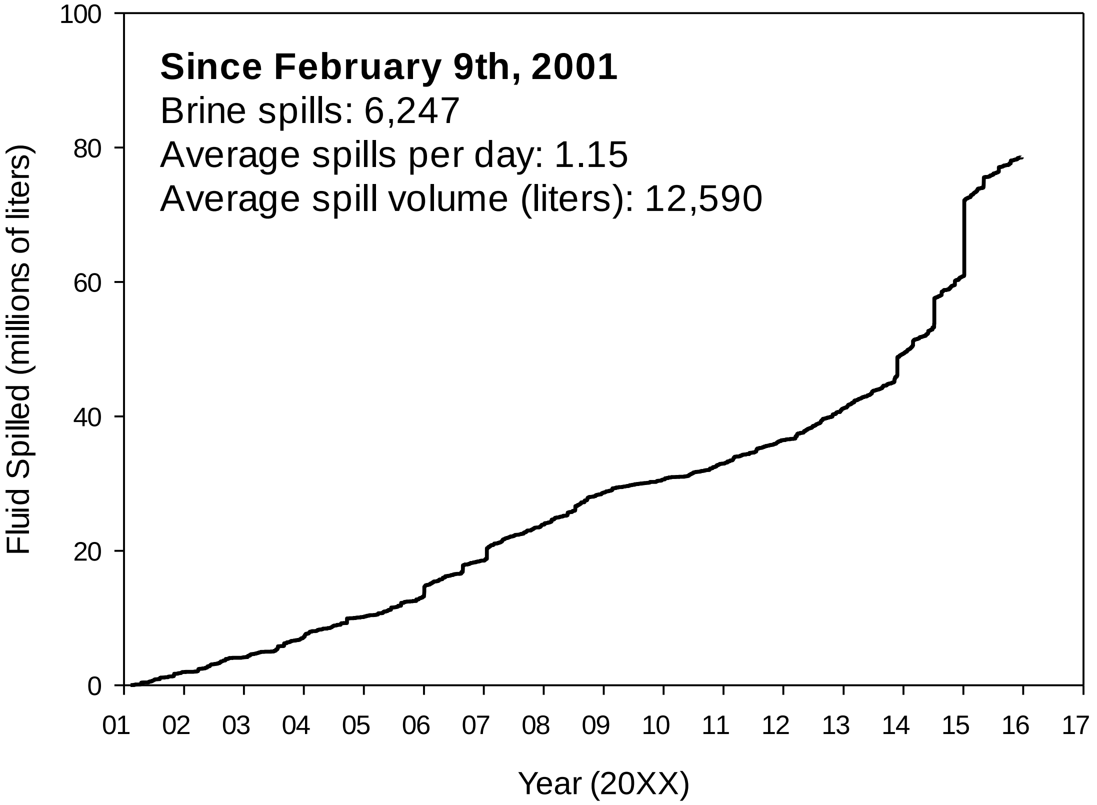

**Figure 3.** Quantity of brine spilled on and off oil drill pads during and after oil and gas exploration efforts in North Dakota from February 9th 2001 through December 23rd 2015 summarized from the North Dakota Department of Health spill database (ND DOH, 2015). The first date coincides with when the North Dakota spill records began reporting the amount of brine spilled.

Many soil EC methods have been assessed in an effort to improve efficiency and reduce costs for determining soil salinity. Determining the extent of salinity using various soil-to-water suspension ratios (e.g., 1:1, 1:2, 1:2.5, 1:5, and 1:10 soil-to-water suspensions) is a more time- and cost-effective method as compared to using the standard saturated paste extract $EC_e$ (He et al., 2012; Sonmez et al., 2008). Remediation strategies for brine spills rely on having accurate, reliable, and timely data so that the spill area can be delineated and contained, and so first-response remediation actions can be made. Currently, most assessment strategies involve using saturated paste extracts, and can take over 48 hr to get results. Using soil-to-water suspensions with shorter equilibration and preparation times will drastically reduce the work and time involved in obtaining soil EC measurements. Soil testing laboratories and land-reclamation consultants in Australia and China commonly use the 1:5 soil-to-water suspensions as well as 1:1 soil-to-water suspensions in the United States and Canada (He et al., 2012; Rayment and Lyons, 2011; Wang et al., 2011; Hogg and Henry, 1984). Sonmez et al. (2008) observed high correlations between $EC_e$ and the EC values of 1:1, 1:2.5, and 1:5 soil-to-water suspensions for soils in Turkey with a slightly better correlation using the 1:2.5 suspension.

Researchers have developed these methods and their conversion equations for naturally salinized soils by ground waters and salt-baring surface geology and not under the conditions of anthropogenic brine contamination. Furthermore, many scientists and environmental consultants determine soil EC of brine-contaminated soils in the field using portable conductivity meters. Most of these meters are limited in their EC measurement range (e.g., 0.1 – 20 dS $m^{-1}$), although brine EC levels often exceed 200 dS $m^{-1}$ (Keiffer and Ungar, 2002). The existing EC methods and conversion equations have been found to be reliable for a wide range of soil textures (sandy, loam, and clayey soils) and $EC_e$ values ranging from 0.1 to 227 dS $m^{-1}$ (Khorsandi and Yazdi, 2011; Chi and Wang, 2010; Ozcan et al., 2006; Zhang et al., 2005; Hogg and Henry, 1984). However, since these conversion equations are calibrated and validated for naturally-occurring soil salinity, the calibration ranges are often limited to $EC_e$ values between 0.1 and 25 dS $m^{-1}$ (He et al., 2012; Sonmez et al., 2007; Ozcan et al., 2006; Hogg and Henry, 1984). The development and validation of conversion equations in the range of $EC_e$ observed in brine spill sites are lacking (Chi and Wang, 2010; Zhang et al., 2005).

One study successfully developed conversion equations for soils with $EC_e$ ranging from 1 to 227 dS $m^{-1}$ for sodium ($Na^+$) based soils (Chi and Wang, 2010). However, their equations do not address an apparent heteroscedasticity as observed in another conversion equation study done on naturally-occurring saline soils by He et al. (2012). Another study on naturally-occurring saline soils observed a strong correlation ($r^2 = 0.98$) between $EC_{1:1}$ and $EC_e$ for medium textured soils with an $EC_e$ ranging from 0.2 to 42.1 dS $m^{-1}$ (Hogg and Henry, 1984). Sonmez et al. (2008) developed equations for converting $EC_{1:1}$, $EC_{1:2.5}$, and $EC_{1:5}$ to $EC_e$ using sandy, loamy, and clayey soils with soil $EC_e$ values ranging from 0.2 to 17.7 dS $m^{-1}$. The soils used by Sonmez et al. (2008) were treated with NaCl, KCl, and $CaCl_2$ solutions. However, conductivity factors are specific to ion species and associations (Tolgyessy, 1993). Therefore, caution should be taken when using conversion equations if the general solution composition is not known.

The reported differences in conversion factors (i.e. the slope factor of a linear model to predict ECe from a soil-to-water suspension) of soil-to-water suspensions between 1:1 and 1:5 range from 3.84 to 5.56 (Sonmez et al., 2008; Ozcan et al., 2006; Zhang et al., 2005; Hogg and Henry, 1984; USDA, 1954). In comparison, soil texture contributes a minimal influence on conversion factors with reported differences among soil textures ranging from 0.05 to 0.86 (Sonmez et al., 2008; Hogg and Henry, 1984). Studies in the United States and Canada indicate no substantial textural influences on conversion factors (Hogg and Henry, 1984). Therefore, evaluating textural influences on conversion equations is not an objective of this study.

The objectives of this study were to 1) determine the magnitude of soil $EC_e$ for non-remediated brine spills in North Dakota, 2) develop conversion equations among soil EC obtained from saturated paste extracts and 1:1 and 1:5 soil-to-water suspensions for the full range of observed soil $EC_e$ observed for objective 1, and 3) determine soil-to-water suspension equilibration times for brine-contaminated soils. Previous studies in the United States and Canada indicate no substantial textural influences on conversion equation parameters (Hogg and Henry, 1984). Therefore, textural influences on conversion equations is not an objective of this study. We hypothesize that a new set of conversion equations can be developed under brine spill conditions that will produce predictions of $EC_e$ with less errors than other equations previously reported in the literature and that do not require previous knowledge of soil texture.

We obtained soil samples across multiple soil depths at seven brine spill sites in North Dakota, ranging in time-since contamination, and determined four logarithmic conversion equations including: 1) conversion of $EC_{1:1}$ to $EC_{1:5}$, 2) conversion of $EC_{1:5}$ to $EC_{1:1}$, 3) conversion of $EC_{1:5}$ to $EC_e$, and 4) conversion of $EC_{1:1}$ to $EC_e$. By developing and validating conversion equations for soil EC values of brine-contaminated soils with a wide range of EC values (i.e., 0 – 126 dS $m^{-1}$) and addressing the issues of heteroscedasticity, our study extends beyond the data currently cited in the scientific literature.

## Materials and Methods

Soil samples (n=110) were collected from seven sites in Bottineau and Burke Co., North Dakota, USA, in August, 2014. Each site was the area of an un-reclaimed brine spill from either recent (i.e., ≤ 5 yr since spill) or from older uncontrolled releases (i.e., > 40 yr since spill). The seven sites varied in soil type (Table 1), brine spill age and size, and historical land use. Soil samples were collected at each site from 0-15, 15-30 and 30-60 cm depths along transects extending within and outside of the brine spill perimeter. Soils taken from each site are classified as smectitic and mixed mineralogy and include sand, sandy clay loam, loam, clay loam, silt loam, and silty clay loam textures (Table 1). After collection, samples were air-dried, ground, and passed through a 2 mm sieve before analysis.

### *1:1 and 1:5 Soil-to-Water Suspensions ($EC_{1:1}$; $EC_{1:5}$)*

The 1:1 and 1:5 soil-to-water suspensions were made by adding together 10 g of soil and 10 mL of deionized (DI) water, and 5 g of soil and 25 mL of DI water, respectively. Then, the soil-to-water suspensions were equilibrated using a slightly modified procedure from He et al. (2015). Each 1:1 and 1:5 suspension was manually stirred for 10 s with a glass stir rod, and allowed to equilibrate for at least 18 h, which is greater than the 8 h recommendation by He et al. (2012). Longer equilibration times were used in this study to ensure complete NaCl dissolution. A subset of soil-to-water suspensions (n = 5) representing a large range of soil salinity were also analyzed for EC using 0, 2, 4, 8, and 18 hr equilibration times to determine if and when an equilibration would occur. Each soil-to-water suspension was stirred with a glass rod for another 10 s before measuring EC. The 1:1 and 1:5 soil-to-water suspension ($EC_{1:1}$ and $EC_{1:5}$, respectively) were then measured for EC using a Sension 378 conductivity probe (Hach Co., Loveland, CO, USA) which has an operating range of 0 to 199.9 dS $m^{-1}$.

**Table 1.** Soil taxonomic information and characteristics of seven brine spill sites in western North Dakota.

| | Site 1 | Site 2 | Sites 3, 4, 5 | Sites 6, 7 |
|---|---|---|---|---|
| Series | Zahl-Williams-Zahill | Hamerly-Tonka | Barnes-Svea-Tonka | Marysland-Divide-Totten |
| Taxonomy[†] (USDA) | Fine-loamy, mixed, superactive, frigid Typic Calciustolls<br>Fine-loamy, mixed, superactive, frigid Typic Argiustolls<br>Fine-loamy, mixed, superactive, frigid Typic Calciustepts | Fine-loamy, mixed, superactive, frigid Aeric Calciaquolls<br>Fine, smectitic, frigid Argiaquic Argialbolls | Fine-loamy, mixed, superactive, frigid Calcic Hapludolls<br>Fine-loamy, mixed, superactive, frigid Pachic Hapludolls<br>Fine, smectitic, frigid Argiaquic Argialbolls | Fine-loamy over sandy or sandy-skeletal, mixed, superactive, frigid Typic Calciaquolls<br>Fine-loamy over sandy or sandy-skeletal, mixed, superactive, frigid Aeric Calciaquolls<br>Fine-loamy over sandy or sandy-skeletal, mixed, superactive, frigid Typic Natraquolls |
| Soil Texture | Loam, Clay Loam | Loam, Silt Loam, Silty Clay Loam | Loam, Silt Loam, Silty Clay Loam | Loam, Sandy Clay Loam, Sand |
| Drainage Class | Well drained | Somewhat poorly drained | Well drained | Poorly drained |
| Annual Precipitation[‡] (cm) | 35.6 | 50.8 | 48.2 | 55.9 |

[†]=Taxonomic descriptions for each series in complex

[‡]=Precipitation is the average for the soil series complex; obtained from soil official series descriptions

### *Saturated Paste Extract ($EC_e$)*

The saturated paste extracts were made by adding together 170 g of soil and DI water as described by Handbook 60 of the United States Department of Agriculture (USDA, 1954). The soil and water mixtures were stirred with a modified drill press until the desired paste consistency was obtained as described in Handbook 60 (USDA, 1954). Similar to the 1:1 and 1:5 suspensions, the saturated pastes were allowed to rest for at least 18 h to reach a state of equilibrium. Extracts from the saturated pastes were acquired using 413 VWR filter paper and a Buechner funnel under an applied vacuum. The electrical conductivities of the $EC_e$ were then determined using a Sension 378 conductivity probe (Hach Co., Loveland, CO, USA). Cation concentrations of the saturated paste extracts for determining sodium adsorption ratio (SAR) (i.e., Na, Ca, and Mg) were measured using an atomic absorption spectrophotometer (Model 200A, Buck Scientific).

### *Equation Development and Validation*

To describe the relationship between each EC extraction method, equations were developed for $EC_e$ vs. $EC_{1:1}$, $EC_e$ vs. $EC_{1:5}$, and $EC_{1:1}$ vs. $EC_{1:5}$ using linear regression on samples obtained from four of the seven spill sites (n = 64). For the equation development, soil samples from all three depths were used from sites 2, 4, 6, and 7 to create equations that were robust enough to represent soils across sites, texture, and sample depth. Site characteristics are described in Table 1. The validation was then performed with soil samples from all three depths from sites 1, 3, and 5. When comparing the raw $EC_e$ values to $EC_{1:1}$ and $EC_{1:5}$, the relationships had an apparent curvilinear trend and heteroscedasticity during linear analysis. Therefore, all EC values were $\log_{10}$ transformed prior to the regression analysis to gain linear relationships with homoscedasticity.  Equations were then developed by

$$\mathbf{EC_e = 10^{a\,(LogEC_{1:1,1:5})+b}} \tag{1}$$

where a and b are fitted regression coefficients. The developed equations were then validated with an independent set of samples from the remaining three of the seven sites (n = 44) using RMSE and bias. The RMSE and bias were determined by

$$\mathbf{RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(EC_i - EC_p\right)^2}} \tag{2}$$

$$\mathbf{bias = \frac{1}{N}\sum_{i=1}^{N}\left(EC_i - EC_p\right)} \tag{3}$$

where N is the number of observations, $EC_i$ is the measured value, and $EC_p$ is the predicted value of $EC_{1:5}$, $EC_{1:1}$, or $EC_e$ based on the derived regression equations 4, 5, 6, and 7. Statistical analyses were performed using PROC Reg. in SAS® statistical software (version 9.4, SAS Institute, Inc., Cary, NC). Nonlinear regression analysis was performed to determine relationships of $EC_e$, $EC_{1:1}$, and $EC_{1:5}$ to Na, Ca, and Mg concentrations in the saturated paste extract using Sigma Plot (version 12.4, Systat Software, Inc., San Jose, CA).

## Results

### *General Soil Properties and Soil EC Extract Relationships*

Soil ECs ranged from 0.2 to 11.5, 0.3 to 23.3, and 0.4 to 126 dS $m^{-1}$ for $EC_{1:5}$, $EC_{1:1}$, and $EC_e$, respectively (Tables 2 and 3). When determining equilibration times for $EC_{1:1}$ and $EC_{1:5}$ values, regression slopes were not significantly different ($P > 0.20$) over time (Figure 4). $EC_{1:1}$ and $EC_{1:5}$ values for all time periods were within the RMSE for the predicted vs. measured $EC_e$, indicating that soil-to-water suspensions can be analyzed for EC directly after 10 s of mixing.

Saturated paste extract $Na^+$ and SAR values ranged from 1 to 828 mmol $L^{-1}$ and 0.3 to 72, respectively (Tables 2 and 3). Saturated paste extract Na was highly correlated with soil $EC_e$, $EC_{1:1}$, and $EC_{1:5}$ values at coefficient of determination ($r^2$) values of 0.91, 0.86, and 0.86,

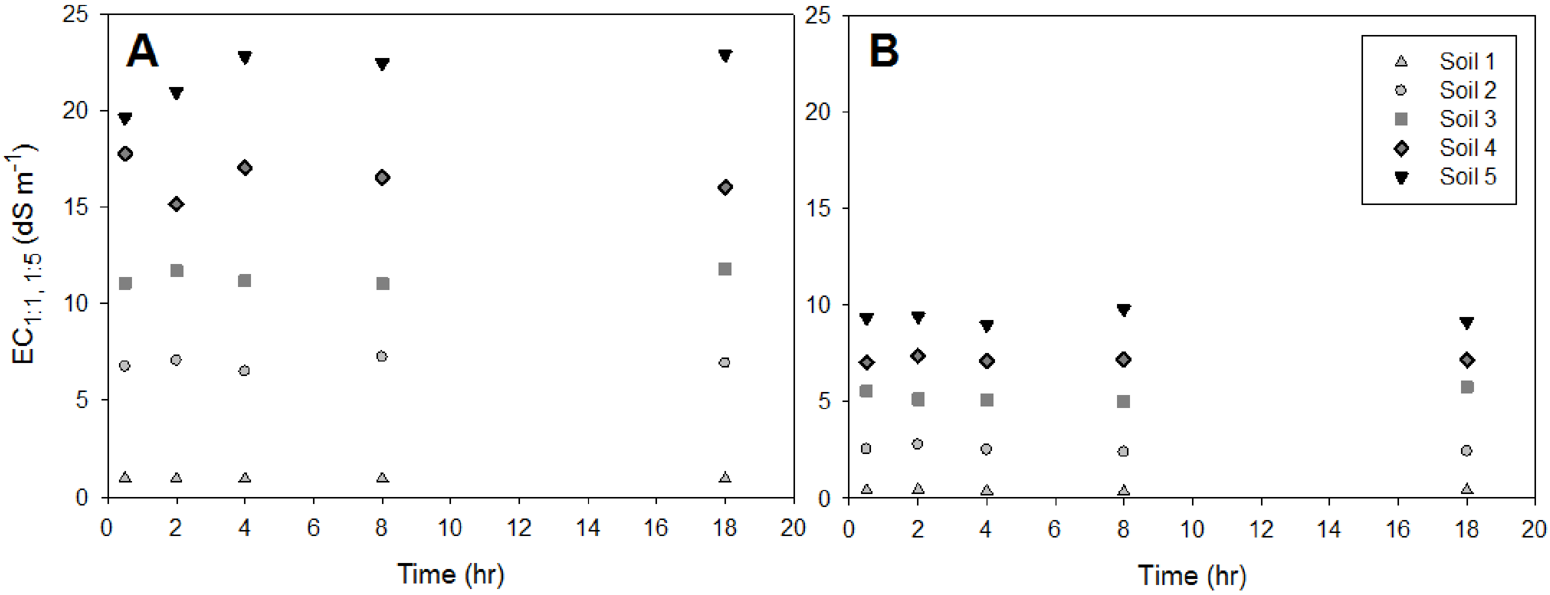

**Figure 4.** Equilibration times for $EC_{1:1}$ and $EC_{1:5}$. Time periods ranged from 0 to 18 hr. Soil EC values did not differ with time ($P > 0.20$). Panels A and B are $EC_{1:1}$ and $EC_{1:5}$, respectively.

**Table 2**. General soil chemical properties for 110 soil samples from western North Dakota based on site

| | | Soil Chemical Property | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Statistic | [†]EC$_{1:1}$ | EC$_{1:5}$ | EC$_e$ | [‡]TDS$_{1:1}$ | TDS$_{1:5}$ | TDS$_e$ | SAR[§] | Na$^+$ | Ca$^{2+}$ | Mg$^{2+}$ |
| | | -------- dS m$^{-1}$ -------- | | | ----------- g L$^{-1}$ ----------- | | | | ----------meq L$^{-1}$---------- | | |
| Site 1 | Mean | 4.02 | 2.15 | 13.3 | 2.57 | 1.37 | 8.49 | 4.47 | 38.7 | 44.7 | 76.6 |
| | Median | 3.25 | 1.94 | 8.42 | 2.08 | 1.24 | 5.39 | 3.15 | 21.4 | 36.3 | 33.0 |
| | Minimum | 1.48 | 0.77 | 3.66 | 0.94 | 0.49 | 2.34 | 0.32 | 2.02 | 24.7 | 8.56 |
| | Maximum | 9.66 | 4.53 | 35 | 6.18 | 2.90 | 22.4 | 11.5 | 116 | 113 | 260 |
| | St. Dev.[ǂ] | 2.63 | 1.27 | 11.3 | 1.68 | 0.81 | 7.22 | 4.10 | 42.2 | 24.9 | 86.7 |
| | Statistic | [†]EC$_{1:1}$ | EC$_{1:5}$ | EC$_e$ | [‡]TDS$_{1:1}$ | TDS$_{1:5}$ | TDS$_e$ | SAR[§] | Na$^+$ | Ca$^{2+}$ | Mg$^{2+}$ |
| | | -------- dS m$^{-1}$ -------- | | | ----------- g L$^{-1}$ ----------- | | | | ----------meq L$^{-1}$---------- | | |
| Site 2 | Mean | 9.38 | 4.11 | 41.5 | 6.00 | 2.63 | 26.5 | 42.4 | 269 | 101 | 36.4 |
| | Median | 6.92 | 3.46 | 23.6 | 4.43 | 2.21 | 15.1 | 45.6 | 198 | 47.7 | 34.6 |
| | Minimum | 4.44 | 1.84 | 14.9 | 2.84 | 1.18 | 9.54 | 15.1 | 99.7 | 5.91 | 4.38 |
| | Maximum | 23.3 | 11.5 | 105 | 14.9 | 7.37 | 67.3 | 71.7 | 785 | 868 | 132 |
| | St. Dev.[ǂ] | 5.19 | 2.56 | 28.7 | 3.32 | 1.64 | 18.4 | 18.0 | 185 | 216 | 31.6 |
| | Statistic | [†]EC$_{1:1}$ | EC$_{1:5}$ | EC$_e$ | [‡]TDS$_{1:1}$ | TDS$_{1:5}$ | TDS$_e$ | SAR[§] | Na$^+$ | Ca$^{2+}$ | Mg$^{2+}$ |
| | | ------- dS m$^{-1}$ ------- | | | ----------- g l$^{-1}$ ----------- | | | | ----------meq L$^{-1}$--------- | | |
| Site 3 | Mean | 10.7 | 4.91 | 52.1 | 6.84 | 3.14 | 33.3 | 28.6 | 304 | 95.7 | 121 |
| | Median | 8.01 | 3.54 | 31.7 | 5.13 | 2.27 | 20.3 | 12.7 | 141 | 76.8 | 120 |
| | Minimum | 4.24 | 2.44 | 16.4 | 2.71 | 1.56 | 10.5 | 7.06 | 71.8 | 50.1 | 54.1 |
| | Maximum | 20.1 | 9.33 | 125 | 12.9 | 5.97 | 79.7 | 70.5 | 828 | 193 | 192 |
| | St. Dev.[ǂ] | 5.56 | 2.52 | 36.1 | 3.56 | 1.61 | 23.1 | 23.1 | 263 | 45.2 | 49.1 |
| | Statistic | [†]EC$_{1:1}$ | EC$_{1:5}$ | EC$_e$ | [‡]TDS$_{1:1}$ | TDS$_{1:5}$ | TDS$_e$ | SAR[§] | Na$^+$ | Ca$^{2+}$ | Mg$^{2+}$ |
| | | ------- dS m$^{-1}$ ------- | | | ----------- g L$^{-1}$ ----------- | | | | ----------meq L$^{-1}$---------- | | |
| Site 4 | Mean | 5.53 | 2.64 | 22.1 | 3.54 | 1.69 | 14.2 | 12.3 | 120 | 64.7 | 44.4 |
| | Median | 2.95 | 1.71 | 7.90 | 1.89 | 1.09 | 5.06 | 4.99 | 24.0 | 30.9 | 32.9 |
| | Minimum | 0.58 | 0.31 | 1.32 | 0.37 | 0.20 | 0.84 | 0.390 | 1.12 | 9.44 | 3.68 |
| | Maximum | 20.9 | 9.28 | 106 | 13.4 | 5.94 | 67.6 | 41.1 | 624 | 353 | 192 |
| | St. Dev.[ǂ] | 5.84 | 2.56 | 29.0 | 3.74 | 1.64 | 18.5 | 14.7 | 181 | 79.8 | 50.5 |
| | Statistic | [†]EC$_{1:1}$ | EC$_{1:5}$ | EC$_e$ | [‡]TDS$_{1:1}$ | TDS$_{1:5}$ | TDS$_e$ | SAR[§] | Na$^+$ | Ca$^{2+}$ | Mg$^{2+}$ |
| | | ------- dS m$^{-1}$ ------- | | | ----------- g L$^{-1}$ ----------- | | | | -----------meq L$^{-1}$---------- | | |
| Site 5 | Mean | 5.33 | 2.50 | 22.1 | 3.41 | 1.60 | 14.1 | 11.6 | 102 | 71.4 | 61.3 |
| | Median | 4.77 | 2.33 | 16.1 | 3.05 | 1.49 | 10.3 | 9.76 | 80.4 | 51.4 | 39.2 |
| | Minimum | 0.34 | 0.16 | 0.41 | 0.21 | 0.10 | 0.26 | 0.53 | 1.08 | 1.51 | 3.93 |
| | Maximum | 16.2 | 7.39 | 78.8 | 10.4 | 4.73 | 50.4 | 23.0 | 330 | 271 | 214 |
| | St. Dev.[ǂ] | 3.87 | 1.67 | 19.6 | 2.48 | 1.07 | 12.5 | 7.96 | 89.3 | 65.3 | 54.5 |
| | Statistic | [†]EC$_{1:1}$ | EC$_{1:5}$ | EC$_e$ | [‡]TDS$_{1:1}$ | TDS$_{1:5}$ | TDS$_e$ | SAR[§] | Na$^+$ | Ca$^{2+}$ | Mg$^{2+}$ |
| | | ------- dS m$^{-1}$ ------- | | | ----------- g L$^{-1}$ ----------- | | | | ---------meq L$^{-1}$---------- | | |
| Site 6 | Mean | 8.45 | 3.63 | 36.8 | 5.41 | 2.32 | 23.6 | 11.4 | 160 | 169 | 123 |
| | Median | 7.16 | 2.86 | 27.5 | 4.58 | 1.83 | 17.6 | 10.4 | 110 | 107 | 86.6 |
| | Minimum | 3.32 | 1.41 | 8.72 | 2.12 | 0.90 | 5.58 | 1.66 | 10.6 | 41.5 | 35.3 |
| | Maximum | 22.9 | 9.13 | 126 | 14.7 | 5.84 | 80.4 | 24.6 | 538 | 646 | 398 |
| | St. Dev.[ǂ] | 6.01 | 2.26 | 34.9 | 3.85 | 1.45 | 22.4 | 8.28 | 171 | 175 | 106 |
| | Statistic | [†]EC$_{1:1}$ | EC$_{1:5}$ | EC$_e$ | [‡]TDS$_{1:1}$ | TDS$_{1:5}$ | TDS$_e$ | SAR[§] | Na$^+$ | Ca$^{2+}$ | Mg$^{2+}$ |
| | | ------- dS m$^{-1}$ ------- | | | ----------- g L$^{-1}$ ----------- | | | | ---------meq L$^{-1}$--------- | | |
| Site 7 | Mean | 5.11 | 2.43 | 18.6 | 3.27 | 1.55 | 11.9 | 6.39 | 56.4 | 77.2 | 74.8 |
| | Median | 4.26 | 1.86 | 14.2 | 2.73 | 1.19 | 9.11 | 2.28 | 17.1 | 59.8 | 38.7 |
| | Minimum | 2.21 | 0.79 | 5.40 | 1.41 | 0.50 | 3.46 | 0.51 | 2.97 | 35.3 | 23.6 |
| | Maximum | 13.8 | 5.8 | 57.9 | 8.83 | 3.71 | 37.1 | 21.4 | 237 | 292 | 312 |
| | St. Dev.[ǂ] | 3.42 | 1.56 | 15.2 | 2.19 | 1.00 | 9.71 | 7.36 | 71.7 | 64.0 | 77.6 |

[†]=Electrical conductivity (EC)

[‡]=Total dissolved solids (TDS). Values estimated from measured soil EC as described by (Rhoades, 1996)

[§]=Sodium adsorption ratio (SAR)

[ǂ]=Standard deviation (St. Dev.)

**Table 3.** General soil chemical properties for 110 soil samples from western North Dakota based on depth

| Depth | Statistic | [†]$EC_{1:1}$ | $EC_{1:5}$ | $EC_e$ | [‡]$TDS_{1:1}$ | $TDS_{1:5}$ | $TDS_e$ | SAR[§] | $Na^+$ | $Ca^{2+}$ | $Mg^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | -------- dS m$^{-1}$ -------- | | | ----------- g l$^{-1}$ ----------- | | | | ------- meq l$^{-1}$ ------- | | |
| 0-15cm | Mean | 8.29 | 3.84 | 37.0 | 5.30 | 2.46 | 23.7 | 17.2 | 191 | 127 | 97.5 |
| | Median | 6.48 | 2.71 | 23 | 4.15 | 1.73 | 14.7 | 9.33 | 94.8 | 61.1 | 51.8 |
| | Minimum | 0.34 | 0.16 | 0.41 | 0.21 | 0.10 | 0.26 | 0.32 | 1.08 | 1.51 | 3.68 |
| | Maximum | 23.3 | 11.5 | 126 | 14.9 | 7.37 | 80.4 | 71.7 | 828 | 868 | 398 |
| | St. Dev.[ǂ] | 6.86 | 3.05 | 38.0 | 4.39 | 1.95 | 24.3 | 20.5 | 243 | 178 | 95.1 |
| | | [†]$EC_{1:1}$ | $EC_{1:5}$ | $EC_e$ | [‡]$TDS_{1:1}$ | $TDS_{1:5}$ | $TDS_e$ | SAR[§] | $Na^+$ | $Ca^{2+}$ | $Mg^{2+}$ |
| | | -------- dS m$^{-1}$ -------- | | | ----------- g l$^{-1}$ ----------- | | | | ------- meq l$^{-1}$ ------- | | |
| 15-30cm | Mean | 5.83 | 2.74 | 23.8 | 3.73 | 1.76 | 15.2 | 15.6 | 119 | 63.6 | 58.0 |
| | Median | 4.44 | 2.24 | 17.1 | 2.84 | 1.43 | 10.9 | 8.30 | 70.2 | 48.9 | 38.3 |
| | Minimum | 0.56 | 0.26 | 0.93 | 0.36 | 0.17 | 0.60 | 0.53 | 1.19 | 5.92 | 3.93 |
| | Maximum | 18.9 | 7.56 | 87.1 | 12.1 | 4.84 | 55.7 | 60.7 | 547 | 266 | 207 |
| | St. Dev.[ǂ] | 4.11 | 1.73 | 22.0 | 2.63 | 1.10 | 14.1 | 17.3 | 136 | 49.4 | 51.2 |
| | | [†]$EC_{1:1}$ | $EC_{1:5}$ | $EC_e$ | [‡]$TDS_{1:1}$ | $TDS_{1:5}$ | $TDS_e$ | SAR[§] | $Na^+$ | $Ca^{2+}$ | $Mg^{2+}$ |
| | | -------- dS m$^{-1}$ -------- | | | ----------- g l$^{-1}$ ----------- | | | | ------- meq l$^{-1}$ ------- | | |
| 30-60cm | Mean | 6.34 | 2.86 | 26.3 | 4.06 | 1.83 | 15.4 | 17.7 | 138 | 65.8 | 62.7 |
| | Median | 5.13 | 2.45 | 19.4 | 3.28 | 1.57 | 10.9 | 12.0 | 85.2 | 51.4 | 42.0 |
| | Minimum | 0.87 | 0.44 | 3.54 | 0.56 | 0.28 | 2.27 | 0.51 | 2.80 | 15.0 | 6.06 |
| | Maximum | 16.2 | 8.00 | 89.7 | 10.4 | 5.12 | 57.4 | 59.9 | 576 | 236 | 217 |
| | St. Dev.[ǂ] | 4.14 | 1.75 | 22.1 | 2.65 | 1.11 | 14.0 | 17.2 | 145 | 52.3 | 50.2 |

[†]=Electrical conductivity (EC)

[‡]=Total dissolved solids (TDS). Values estimated from measured soil EC as described by (Rhoades, 1996)

[§]=Sodium adsorption ratio (SAR)

[ǂ]=Standard deviation (St. Dev.)

respectively (Figure 5). In contrast, saturated paste extract Ca and Mg correlated poorly to all three soil EC methods with $r^2$ values ranging from 0.42 to 0.55 and 0.25 to 0.28, respectively (Figure 5).

The relationships among EC extract methods had $r^2$ values of 0.97, 0.97, and 0.91 for $EC_{1:1}$ vs. $EC_{1:5}$, $EC_e$ vs. $EC_{1:1}$, and $EC_e$ vs. $EC_{1:5}$, respectively, with RMSE's ranging from 0.06 to 0.10 (Figures 6 and 7). Based on these analyses, soil $EC_e$ can be accurately estimated from a measured $EC_{1:1}$ and $EC_{1:5}$ value across a large range (i.e., 0 to 126 dS $m^{-1}$) using the following equations:

$$\boldsymbol{EC_{1:5} = 10^{0.9749(LogEC_{1:1}) - 0.3122}} \tag{4}$$

$$\boldsymbol{EC_{1:1} = 10^{1.0257(LogEC_{1:5}) + 0.3202}} \tag{5}$$

$$\boldsymbol{EC_{e} = 10^{1.2562(LogEC_{1:5}) + 0.7659}} \tag{6}$$

$$\boldsymbol{EC_{e} = 10^{1.2533(LogEC_{1:1}) + 0.3533}} \tag{7}$$

### *Validation of Equations*

The above conversion equations were validated against an independent dataset of different soils from the three remaining sites not used in developing and calibrating the equations (Figures 6 and 7). Validation RMSE values ranged from 1.8 to 15 and 4.2 to 16 dS $m^{-1}$ using $EC_{1:1}$ and $EC_{1:5}$ values, respectively. Overall RMSE for $EC_{1:1}$ and $EC_{1:5}$ values were 6.1 and 7.6 dS $m^{-1}$, respectively. Bias values were 2.57, 2.31 and -0.18 dS $m^{-1}$ for $EC_{1:1}$ vs. $EC_e$, $EC_{1:5}$ vs. $EC_e$, and $EC_{1:1}$ vs. $EC_{1:5}$, respectively. RMSE and bias values became larger as measured $EC_e$ increased. Estimates for converting to saturated paste ($EC_e$) values using a 1:1 soil-to-water ratio had the lowest RMSE values (Figure 6). This indicates that $EC_{1:1}$ estimates were closer to the measured data than the $EC_{1:5}$ estimates. During the validation, an underestimation of $EC_e$ values tended to occur for soils with EC and SAR values greater than 85 dS $m^{-1}$ and 60, respectively.

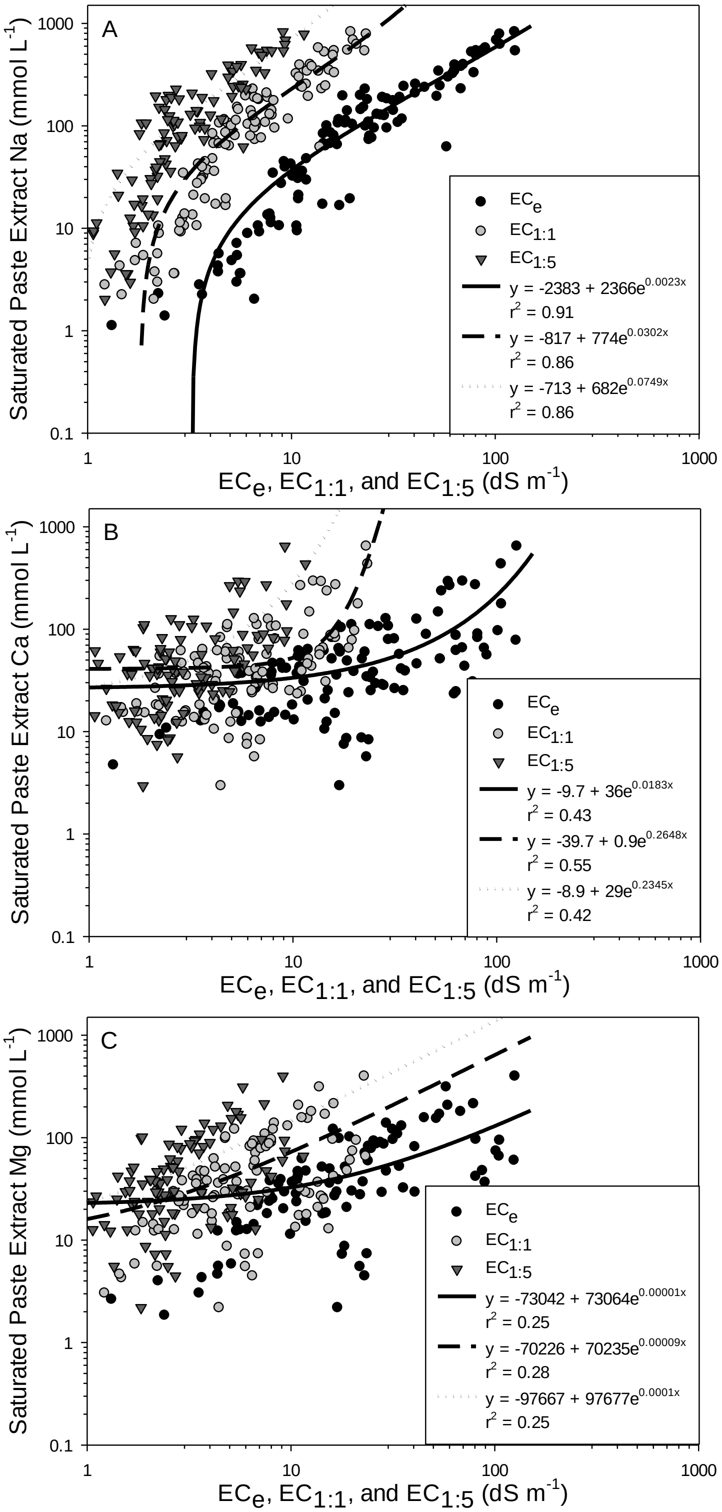

**Figure 5.** Saturated paste extract Na, Ca, and Mg (Panels A, B, and C, respectively) and their relationships to EC$_e$, EC$_{1:1}$, and EC$_{1:5}$.

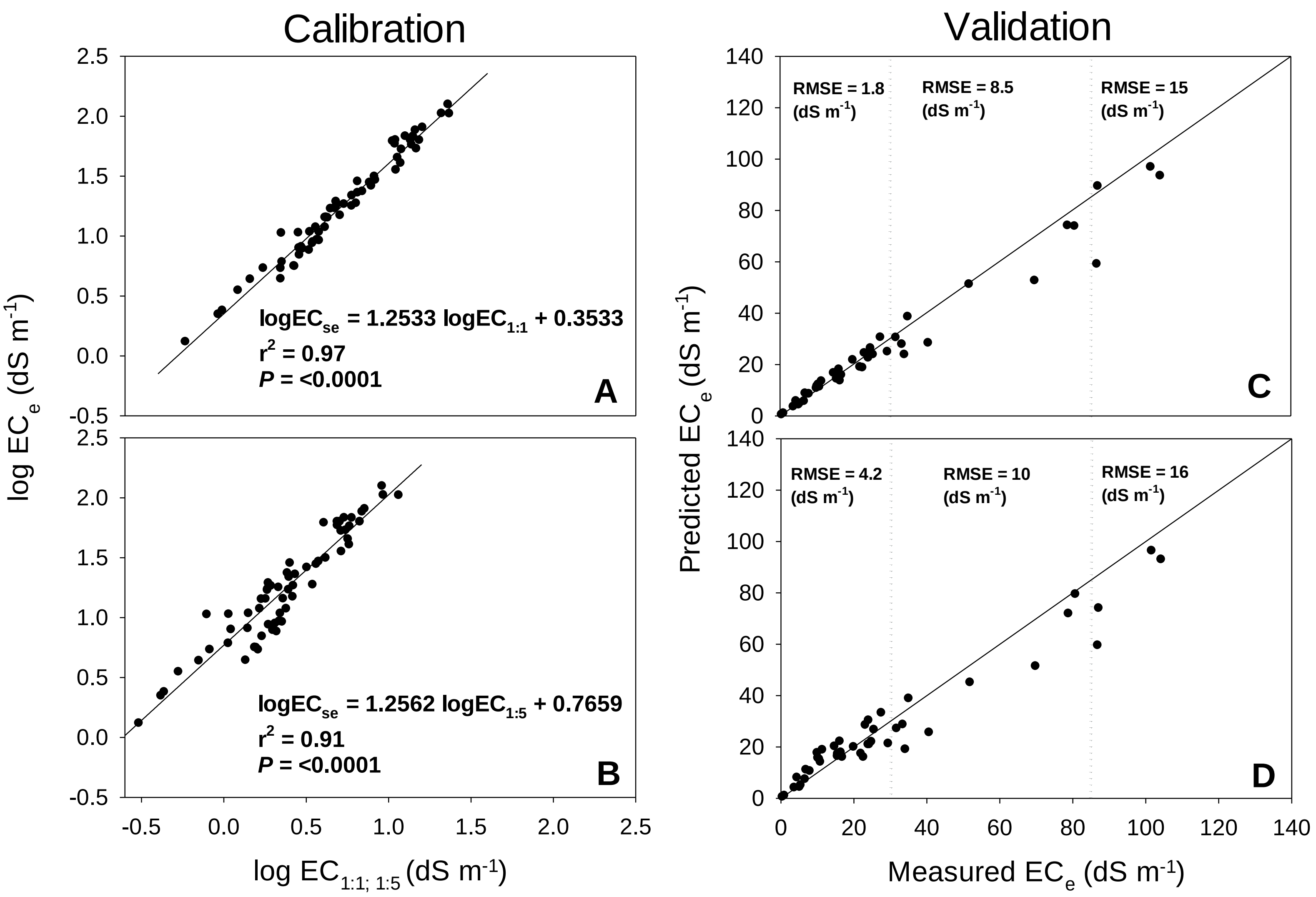

**Figure 6.** Equation development and validation for EC$_e$ vs. EC$_{1:1}$ and EC$_{se}$ vs. EC$_{1:5}$. Panels A and B are the equation developments for EC$_e$ vs. EC$_{1:1}$ and EC$_e$ vs. EC$_{1:5}$, respectively. Panels C and D are the validations for EC$_{1:1}$ and EC$_{1:5}$ conversion equations, respectively.

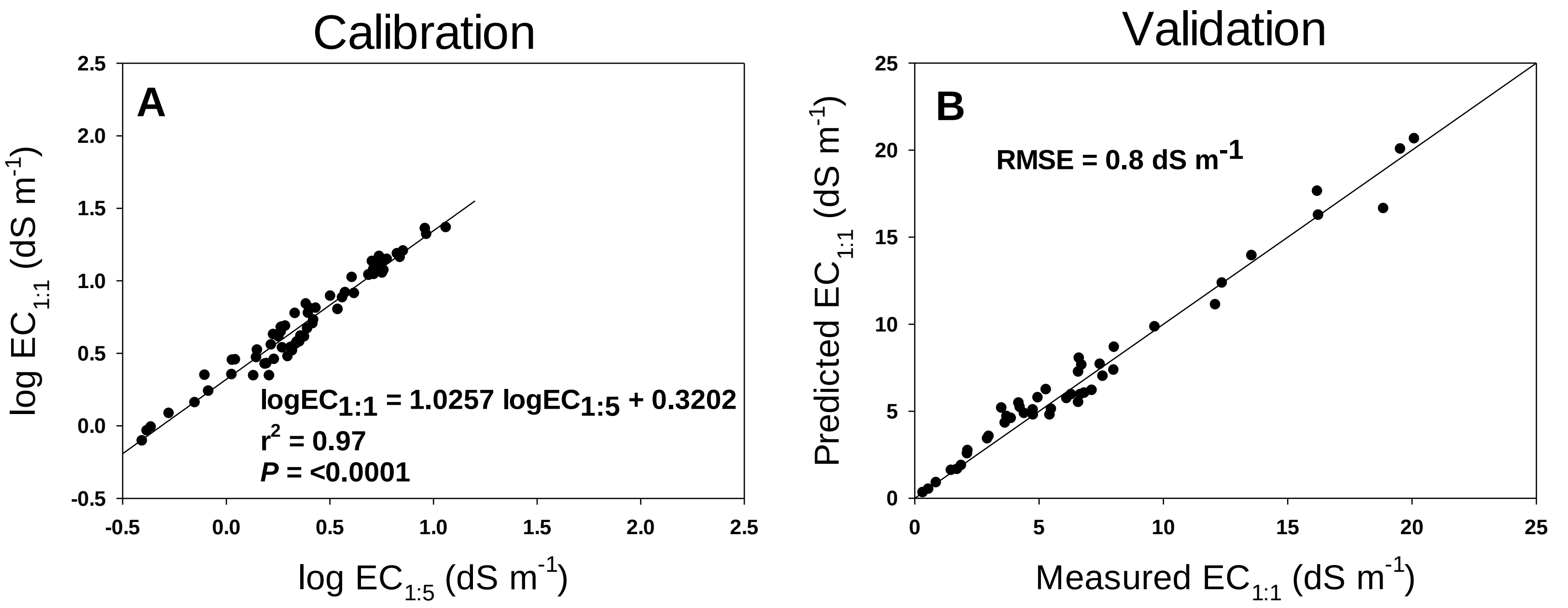

**Figure 7.** Equation development and validation for $EC_{1:1}$ vs. $EC_{1:5}$. Panel A is the equation development for $EC_{1:1}$ vs. $EC_{1:5}$. Panel B is the validation for the $EC_{1:5}$ conversion equation.

## Discussion

Similar to the results reported here, He et al. (2012) observed curvilinear trends while comparing soil EC methodologies. They developed a natural log transformed equation [$EC_e = e^{0.70(\ln EC_{1:5}) +1.78}$] for converting between $EC_{1:5}$ and $EC_e$ in $Ca^{2+}$ and $SO_4^{2-}$ based soils with naturally occurring salinity. In contrast, Chi and Wang (2010) observed relationships between $EC_{1:5}$ and $EC_e$ ($r^2 = 0.94$) for $Na^+$ based soils of China, but did not consider issues of heteroscedasticity in their analysis.

Our newly developed equations were compared with 14 equations derived from eight other EC conversion studies (Figure 8). The same validation data set, as mentioned previously, was used for the comparisons. Among the equations developed here and the other 14 equations reported in the literature, our $EC_{1:1}$ and $EC_{1:5}$ conversion equations were the most accurate followed by the 1:5 soil-to-water ratio equation developed by Chi and Wang (2010) ($r^2=0.94$) at predicting $EC_e$ on brine-contaminated soils based on RMSE values. This was expected since Chi and Wang (2010) used soils with similar $Na^+$ content as the current study to develop their EC conversion equation. Therefore, their $EC_e$ is also likely to be highly correlated with Na content as in the present study (Figure 5).

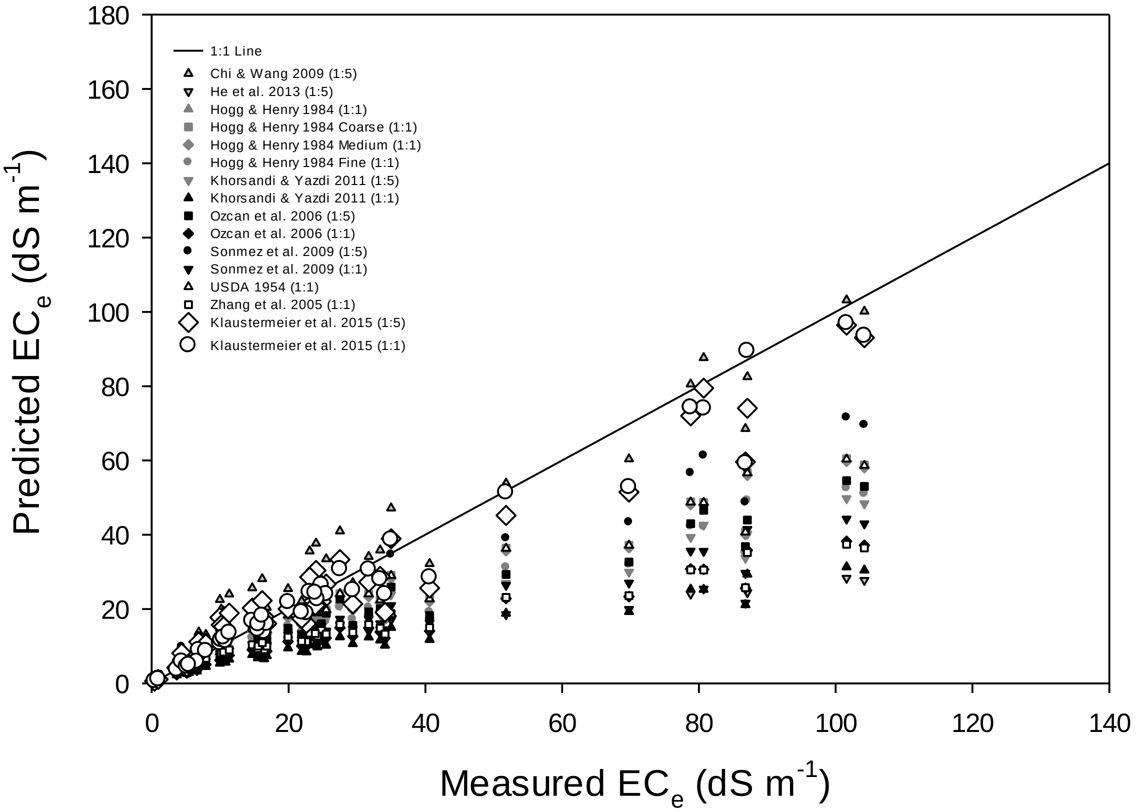

**Figure 8.** Comparison of 14 developed $EC_e$ conversion equations from eight previous soil salinity studies to those developed in this study. Measured values are from a set of 44 validation soil samples. Circles (gray and black) indicate $EC_e$ predictions based on our newly developed $EC_{1:5}$ and $EC_{1:1}$ conversion equations.

Although the Chi and Wang (2010) equation performed well at high and low $EC_e$ values, the equation substantially overestimated $EC_e$ values in the 5 to 35 dS $m^{-1}$ range, whereas our equations did not. As mentioned previously, their overestimations are likely due to the lack of homoscedasticity during their analysis. Equations developed by Hogg and Henry (1984), Khorsandi and Yazdi (2011), and He et al. (2012) were the least accurate at predicting $EC_e$ from $EC_{1:1}$ and $EC_{1:5}$ values, with RMSE of 27.4, 24.6, and 27.3 dS $m^{-1}$, respectively. In contrast, Chi and Wang (2010) and our new equations for predicting $EC_e$ from $EC_{1:1}$ and $EC_{1:5}$ values were the most accurate, with RMSE of 7.63 and 6.13 to 7.62 dS $m^{-1}$, respectively (Table 4). With the

**Table 4.** Comparison of 14 developed EC conversion equations to $EC_{1:5}$ and $EC_{1:1}$ equations developed in this study

| Study | Equation | $r^2$ | RMSE[†] | Soil Description | $EC_e$ Range[‡] |
|---|---|---|---|---|---|
| Chi & Wang (2010) | $EC_e = 11.68(EC_{1:5}) – 5.77$ | 0.94 | 7.63 | Sandy, Loam, Clay | 1 – 227 |
| He et al. (2012) | $EC_e = e^{0.70 \ln (EC_{1:5}) + 1.78}$ | 0.94 | 27.3 | Sandy, Loam, Clay | 0 – 20 |
| Hogg & Henry (1984) | $EC_e = 1.56(EC_{1:1}) – 0.06$ | 0.96 | 27.4 | Sandy, Loam, Clay | 0.10 – 42.0 |
| Hogg & Henry (1984) | $EC_e = 3.01(EC_{1:1}) + 0.06$ | 0.96 | 15.9 | Sandy | 0.10 – 22.4 |
| Hogg & Henry (1984) | $EC_e = 3.01(EC_{1:1}) – 0.77$ | 0.96 | 16.3 | Loam | 0.25 – 42.0 |
| Hogg & Henry (1984) | $EC_e = 2.66(EC_{1:1}) – 0.97$ | 0.96 | 19.1 | Clay | 0.28 – 25.7 |
| Khorsandi & Yazdi (2011) | $EC_e = 5.40(EC_{1:5}) – 0.61$ | 0.94 | 20.5 | Sandy, Loam, Clay | 0.48 – 171 |
| Khorsandi & Yazdi (2011) | $EC_e = 1.56(EC_{1:1}) – 0.06$ | 0.96 | 27.4 | Sandy, Loam, Clay | 0.48 – 171 |
| Sonmez et al. (2007) | $EC_e = 7.68(EC_{1:5}) – 0.16$ | 0.94 | 12.9 | Sandy, Loam, Clay | 0.22 – 17.7 |
| Sonmez et al. (2007) | $EC_e = 2.23(EC_{1:1}) – 0.58$ | 0.96 | 22.3 | Sandy, Loam, Clay | 0.22 – 17.7 |
| Ozcan et al. (2006) | $EC_e = 5.97(EC_{1:5}) – 1.17$ | 0.94 | 18.9 | N/A[§] | N/A |
| Ozcan et al. (2006) | $EC_e = 1.93(EC_{1:1}) – 0.57$ | 0.96 | 24.7 | N/A | N/A |
| USDA (1954) | $EC_e = 3.00(EC_{1:1})$ | 0.96 | 15.9 | N/A | N/A |
| Zhang et al. (2005) | $EC_e = 1.79(EC_{1:1}) + 1.46$ | 0.96 | 24.6 | N/A | 0.1 – 108 |
| Klaustermeier et al. (2016) | $EC_e = 10^{1.2562 \log (EC_{1:5}) + 0.7659}$ | 0.91 | 7.62 | Sandy, Loam, Clay | 0.4 – 126 |
| Klaustermeier et al. (2016) | $EC_e = 10^{1.2533 \log (EC_{1:1}) + 0.3533}$ | 0.97 | 6.13 | Sandy, Loam, Clay | 0.4 – 126 |

[†] = Root mean square error (RMSE) values reported in dS $m^{-1}$

[‡] = Electrical Conductivity (EC) values reported in dS $m^{-1}$

[§] = Data not available

exception of the Chi and Wang (2010) equation, all other equations produced RMSE of 2 to 4.5 times greater than those observed for the equations 6 and 7 presented in this study.

These differences in RMSE among equations are likely due to the soils of other studies being dominated by calcium, magnesium, and sulfate based salts and therefore different ion associations as compared to the soils evaluated in this study. Solutions with more ion associations have less conductivity because they have more neutral ion species complexes and less free species with positive charge (Alzubaidi and Webster, 1983). Sulfate based salts have a high capacity to pair with other cations compared to NaCl-based salts (Essington, 2004). All other equations were somewhat accurate at low $EC_e$ values, but then consistently underestimated $EC_e$ as values increased. It is apparent from these under- and over-estimations that the previously established EC conversion equations reported in the literature are not reliable for estimating $EC_e$ of brine affected soils (i.e. soils with $EC_e$ highly correlated to NaCl salts). In contrast, the conversion equations developed in this study are a significant improvement for predicting $EC_e$ from $EC_{1:1}$ and $EC_{1:5}$ values for brine-contaminated soils than previous equations reported in the literature.

Researchers and land managers can make any of these soil-to-water suspensions with equal time and effort. The equal effort to make the suspensions and the high correlation of all soil-to-water suspension to $EC_e$ demonstrate the arbitrary nature of each soil-to-water ratio. Although arbitrary, errors can occur in predicting $EC_e$ as the difference between soil and water in suspensions increases if suspensions are prepared by increasingly smaller soil quantity.  In other words, if the soil sample used to create a suspension decreases below a representative soil sample, then repeatability of the results is sacrificed.

Soil textural differences can affect soil EC values in soil-to-water suspensions (Hogg and Henry, 1984; Sonmez et al., 2008). As expected, small differences were seen in RMSE values when using previously published EC conversion equations based on texture with our measured $EC_e$, $EC_{1:1}$ and $EC_{1:5}$ values (Table 4). The RMSE values for coarse, medium and fine textured soil equations developed by Hogg and Henry (1984) varied by only 6 and 18%, respectively (Table 4). Improvements in conversion equation accuracy might be gained by differentiating soils by texture; however, these potential improvements do not appear to be warranted for the soils used in this study. The new conversion equations presented here reduced errors by 2 to 4.5 times as compared to other equations reported in the literature without the need for prior knowledge of the soil texture.

These new conversion equations will be applicable to soils contaminated with NaCl-dominated brines as well as NaCl-based naturally-occurring soil salinity due to deep ground water seeps. Since these equations are valid for soil $EC_e$ from 0.4 to 126 dS $m^{-1}$, they can be used for soils classified as both saline and non-saline. However, if brine-contaminated soils contain significant quantities of other dissolved salts (e.g., $Ca^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$ based salts) and the EC is not well correlated with NaCl, then ion pairing can result in conductivity factors that differ from NaCl. In these cases, the new conversion equations may over-estimate $EC_e$ and not be applicable for such soils (Table 4; Figure 8).

## Conclusions

The relationships between all EC methods were highly correlated ($r^2$=0.91 to 0.97, *P*<0.0001), indicating strong evidence that $EC_e$ of soils contaminated with NaCl-dominated brine can be accurately estimated from $EC_{1:1}$ and $EC_{1:5}$ values using the newly developed conversion equations in this study. Based on model validations, using $EC_{1:1}$ to convert to $EC_e$ had the smallest RMSE values. Therefore, if possible, the $EC_{1:1}$ method should be used when evaluating soil salinity levels. Although, both $EC_{1:1}$ and $EC_{1:5}$ equations reduced errors by 2 to 4.5 times as compared to other conversion equations listed in the scientific literature. Additionally, $EC_{1:1}$ and $EC_{1:5}$ values did not significantly change as equilibration times increased after the initial mixing of water and soil. The $EC_{1:1}$ and $EC_{1:5}$ values for all time periods were within the RMSE for the predicted vs. measured $EC_e$, indicating that accurate measurements of $EC_{1:1}$ and $EC_{1:5}$ can be obtained immediately after 10 s of mixing. These newly derived equations and equilibration times will allow environmental consultants, remediation specialists, and research scientists to assess the salinity of brine-contaminated soils more accurately and timely than previous equations reported in the literature.

In summary, soil salinity from NaCl-based brine contamination, or naturally occurring soil salinity that is highly correlated with Na, can be accurately assessed for $EC_e$ values between 0 and 126 dS $m^{-1}$ using the $EC_{1:1}$ and $EC_{1:5}$ methods and conversion equations presented here. These methods require minimal time between mixing of soil-to-water suspensions and subsequent measurement with an EC meter. Future research should include the evaluation of soils where $EC_e$ is strongly correlated with multiple ions. Such soils could represent naturally occurring saline areas innately influenced by Ca, Mg, and $SO_4^{2-}$ based salts that then are subject to NaCl-based brine contamination.

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# SALT EXTRACTION FROM BRINE-CONTAMINATED SOILS AMENDED WITH A CRYSTALLIZATION INHIBITOR[1]

## Abstract

Produced water (NaCl-based brine) contamination of soils is an issue of great concern in areas of oil and gas exploration. Many remediation methods have limited success in reducing salt contamination and allowing vegetation regrowth. However, crystallization inhibitors have been reported to suppress salt damage in ridged porous media (i.e., building materials and stones) by limiting subflorescence and promoting efflorescence on the material’s outer surfaces. We hypothesize that crystallization inhibitors can produce harvestable salt efflorescence from brine-contaminated soils (a soft porous media). The main objectives of this study were to 1) determine if the application of a crystallization inhibitor (ferric hexacyanoferrate) to soil can extract salts and have success as an in-situ remediation method on salt-contaminated soils and 2) determine if the migration and growth of salts are a function of crystallization inhibitor concentration, application method, salt type and soil texture. In a series of laboratory experiments, different concentrations (0.01 to 0.00001M) of ferric hexacyanoferrate were applied to salt-contaminated soil columns using three methods of application and allowed to incubate for seven days after

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[1] The material in this chapter was co-authored by Aaron Klaustermeier, Aaron Daigh, Ryan Limb, and Kevin Sedivec. Aaron Klaustermeier had primary responsibility for analyzing lab samples and for conducting statistical analysis. Aaron Klaustermeier was the primary developer of the conclusions that are advanced here. Aaron Klaustermeier also drafted and revised all versions of this chapter. Aaron Daigh served as proofreader and checked the math in the statistical analysis conducted by Aaron Klaustermeier. This manuscript will be submitted to Environmental Science and Technology.

observing initial efflorescence. Between 29 and 57% of the applied salts effloresced and were accessible for harvesting when a 0.01M concentration of the crystallization inhibitor was surface applied to NaCl-contaminated sandy loam, loam and silty clay soils. Negligible quantities of salts were harvested when the crystallization inhibitor was incorporated into the soil, when the two lowest concentrations were applied regardless of application method, or when the soils were contaminated with sulfate-based salts. Additionally, sequential salt extraction following initial salt harvest was not obtained solely by water reapplication. Based on these results, the in-situ application of ferric hexacyanoferrate appears to be feasible for remediating brine-contaminated soils. Future studies should include salt-specific crystallization inhibitor application, optimal conditions for sequential salt extraction after initial harvest, and in-field testing to further determine the efficacy of crystallization inhibitors as an in-situ remediation amendment.

## Introduction

Areas of oil and gas exploration experience soil salinization when drilling-produced waters (i.e., NaCl brines) spill or leak (Keiffar and Ungar, 2002). Since 2001, brine spill reports in North Dakota average 18 per week, with some pipeline leaks spilling over 4 million liters of brine (ND DOH, 2015). Traditional methods for remediating spill-affected areas include the in-situ method of leaching salts below the plant root zone and the ex-situ method of disposing of contaminated soils in landfills and replacing the excavated area with local topsoil (Gawel, 2006; Harris et al., 2005; Vavrek et al., 2004; Halvorson and Lang, 1989; De Jong, 1982; Jury and Weeks, 1978). However, the end results and duration associated with traditional methods often provide disappointing results. The development of more efficient and rapid response remediation methods is needed in order to remediate these brine-affected lands.

Brine produced throughout North Dakota is comprised mainly of dissolved sodium ($Na^+$) and chloride ($Cl^-$) based salts (90%; McMillion, 1965; Doll et al., 1989), and is a regulated byproduct in the oil and gas industry (Herkelrath et al., 2007). Once produced, drill operators typically dispose of brine through deep injection wells; though improper handling and accidental leaks may lead to the contamination of land and water resources. Brines produced throughout North America typically contain a total dissolved solids (TDS) concentration greater than 100,000 mg $L^{-1}$ with electrical conductivities (EC) > 200 dS $m^{-1}$ (Dresel and Rose, 2010; Sublette et al., 2007; Jury and Weeks, 1978; Latta, 1963). Soil salinity resulting from brine migration off well pads or from breaches in containment walls or beams leads to overall land degradation (Barzegar et al., 1997; Murphy et al., 1988). State government agencies in North Dakota report > 78 million liters of spilled brine associated with oil exploration and drilling in the last 15 years (ND DOH, 2015). Salts from the spills will remain in the soil for decades in absence of remediation, thus reducing plant productivity and innate ecosystem services (Murphy et al., 1988).

Numerous remediation options are available to restore vegetative growth on brine-affected soils, including ex-situ (off-site) or in-situ (on-site) methods. A common ex-situ method involves excavation and disposal of the contaminated soil (commonly referred to as dig-and-haul). Remediation specialists often recommend the dig-and-haul method when the contamination is concentrated either within a small area or near surface and groundwater resources (Harris et al., 2005). This method quickly alleviates the potential for spilled brine to further contaminate adjacent areas; its primary appeal for remediation specialists and consultants. However, the method is invasive and the contaminated soil requires disposal at a waste facility. Common in-situ methods involve the incorporation of divalent-ion based products and organic matter followed by leaching waters to flush salts below the plant root zone (Gawel, 2006; Amezketa, 2005; Harris et al., 2005; Vavrek et al., 2004; Knox and Sabatini, 2000; Ashworth et al., 1999; Atalay, 1999; Halvorson and Lang, 1989; De Jong, 1982; Jury and Weeks, 1978). These chemical amendments are effective only to the depth at which they are applied (Sublette et al., 2007; Robbins, 1986) and large amounts of water and time (1 to > 1000 years) are required to be effective (Jury and Weeks, 1978). Furthermore, in-situ methods may have limited long-term success due to the possibility of soil re-salinization from the translocation of salts to the soil surface due to capillary rise (Hayashi, 1998; Thimm, 1990). A more ideal remediation method would involve permanently removing salts from the affected site while avoiding the degradation of deeper soil horizons.

Previous studies tested the use of crystallization inhibitors on different types of porous stone to determine their ability to reduce damage and subsequently preserve important landmarks across the world (Gupta et al., 2012; Rivas et al., 2010; Lubelli and van Hees, 2007; Rodriguez-Navarro et al., 2002; Selwitz and Doehne, 2002). Salts found within these materials crystallize and begin to grow within the pore network as evaporation occurs and exert pressure within the stone on pore walls, which can lead to damage over time. Crystallization inhibitors are used to prevent salt crystal formation and change salt crystallization growth habits to where the salts effloresce as dendritic formations on the porous media’s outer surfaces (Franceschini et al., 2015; Bode et al., 2012; Cassar et al., 2008). Previous studies tested sodium and potassium hexacyanoferrate ($Na_4[Fe(CN)_6$ and $K_3[Fe(CN)_6]$ and]) as crystallization inhibitors on various types of stone (Gupta et al., 2012; Rivas et al., 2010; Lubelli and van Hees, 2007; Rodriguez-Navarro et al., 2002; Selwitz and Doehne, 2002). After the crystallization inhibitors were applied, NaCl crystals grew upwards on the stone surface rather than internally, producing raised crystallized salt structures, or efflorescence.

Daigh and Klaustermeier (2016) recently demonstrated the use of crystallization inhibitors for harvesting salts from the soil surface of NaCl-based brine-affected soils. When using a 0.01 M solution of ferric hexacyanoferrate ($C_{18}Fe_7N_{18}$) with liquid ammonia, they were able to extract upwards of 0.57 g $g^{-1}$. Aqueous ammonia was used as a solvent to dissociate the Fe ions from the crystallization inhibitor compound and to increase surface evaporation. Extracting salts from the soil surface would be a more permanent solution in reducing salinity on brine-affected areas. Rather than displacing salts downward temporarily, the use of a crystallization inhibitor would work with the natural processes of the soil and evaporative fluxes, allowing salts to migrate upward and be harvested on the surface. Furthermore, the use of crystallization inhibitors as an in-situ remediation method on brine-affected soils would significantly reduce the time associated with other physical or chemical remediation amendments.

The objectives of this study were to determine if 1) a crystallization inhibitor ($Fe_4\,[Fe\,(CN)_6]_3$) will disrupt salt crust formation at the soil surface and instead promote dendritic salt formations above the soil surface, and 2) the mass of salt efflorescence and the subsurface upward migration of salts are a function of crystallization inhibitor concentration, application method, and soil and salt type. The study consisted of three laboratory soil column experiments with the goal of developing and optimizing a brine-spill rapid response method to remove infiltrated waste brine from soils. The broader impacts of such rapid-response remediation options will include reducing risk of $Cl^-$ contamination to shallow ground waters, salinization of adjacent soils due to $Cl^-$ migration, transfer of brine-derived heavy metals in the food chain, re-salinization of surface soils, and remediation closure timelines.

## Materials and Methods

### ***General Column Setup and Soil Description***

Three laboratory column experiments were conducted using ground, homogenous sandy loam, loam, and silty clay soils in a total combined 150 polyvinyl chloride columns (7.7 cm diameter and 10 cm height dimensions). Experiment I determined optimal crystallization inhibitor concentrations and application methods among different soil textures. Experiment II was conducted to determine if a sequential application of either deionized water or a crystallization inhibitor solution will allow greater amounts of harvestable salt extractions from the soil surface after initial salt harvest. Experiment III determined if the application of a crystallization inhibitor can be used to extract other salt species that cause natural soil salinity. The bottom of each soil column was sealed with Plexiglas to prevent the loss of solution and solutes. The sandy loam, loam, and silty clay soils were extracted from the field at the 0-6 cm depth and are classified as a coarse-loamy, mixed, superactive, frigid Aeric Calciaquoll; fine-loamy, mixed, superactive, frigid Typic Argiustoll; and fine, smectitic, frigid Typic Epiaquert, respectively (USDA, 2016). Average $EC_e$ and pH for the soils were 1.18, 0.66, and 0.63 dS $m^{-1}$ and 4.9, 4.7, and 7.6, respectively. Soil series names are Wyndmere, Williams, and Fargo (USDA, 2016).

Salt-saturated solutions were made with deionized (DI) water (pH = 7.81; EC = 0.01 dS $m^{-1}$) in the laboratory using NaCl (6 M) for Experiments I and II, and $Na_2SO_4$ (anhydrous; 1 M), $MgSO_4$ (anhydrous; 3 M) and $CaSO_4$ (dihydrate; 0.01 M) for Experiment III. The crystallization inhibitor used in this study was hexacyanoferrate in the mineral form of ferric hexacyanoferrate

($Fe_4 [Fe (CN)_6]_3$); commonly known as Prussian Blue (Alfa Aesar, Ward Hill Massachusetts, USA). This mineral form is near kinetically inert and requires a solvating agent to decompose to the reaction product hexacyanoferrate (Daigh and Klaustermeier, 2016; Meeussen, et al., 1992; Sharpe, 1976). The mineral form was applied as either 0.00001, 0.0001, 0.001, or 0.01 M suspensions depending on the experiment and treatment. Aqueous ammonia (1.0 % by weight; ammonium hydroxide) was added to each suspension to solvate the crystallization inhibitor into four free Fe ions and three $Fe(CN)_6$ complexes as well as enhance evaporative fluxes in order to stimulate salt efflorescence nucleation (Daigh and Klaustermeier, 2016; Fernelius and Johnson, 1928). Application methods included 1) mixing NaCl with the crystallization inhibitor and ammonia solution and surface applying it to the soil (T1), 2) adding a surface application of saturated NaCl solution to the soil, letting salts crystallize forming a soil crust, and then adding a surface application of the crystallization inhibitor and ammonia solution (T2), and 3) mechanically incorporating and homogenizing the NaCl, crystallization inhibitor, and ammonia solution into the soil (T3). These application methods were chosen to represent a crystallization inhibitor used as a premixed, cautionary method (T1) for NaCl-based brine spills and as two post-spill remediation methods (T2 and T3). All soil columns, besides the controls, had crystallization inhibitor and ammonia solutions applied to them in a constant temperature room (temperature 20.7 ± 0.29°C, relative humidity 22.5 ± 1.59%) and were allowed to evaporate seven days after visual evidence of efflorescence for all experiments.

### *Experiment I - Optimizing Concentrations and Application Methods among Soil Texture*

To optimize the crystallization inhibitor loading rate and application method for various soil textures, the four concentrations of crystallization inhibitor (0.00001, 0.0001, 0.001, and 0.01 M) of the mineral form were applied to NaCl-contaminated soils (i.e., the sandy loam, loam, and silty clay) using the T1, T2, and T3 methods of application. Two soil columns (i.e., two replicates) of each crystallization inhibitor concentration by application method by soil texture combination were used for comparisons, totaling seventy-two columns. For the T1 and T3 columns, 34.75 g of NaCl, the crystallization inhibitor, and 20 mL of aqueous ammonia were added to 110 mL of DI water. This salt, crystallization inhibitor, and ammonia solution was then applied to the soil columns. After seven days of salt efflorescence, the salt formations were hand harvested and the soil columns dissected into 0-3 and 3-6 cm depths for further analysis. The T2 columns initially received a 110 mL surface application of the NaCl-saturated salt solution without the crystallization inhibitor or the aqueous ammonia. After the initial 110 mL application of NaCl solution, a salt crust had formed at and within the first few millimeters of the soil surface. After the seven days, columns received a second 130 mL solution, this time with the crystallization inhibitor and aqueous ammonia but without additional salts. The salt crust initially prevented the crystallization inhibitor and aqueous ammonia solution from infiltrating and instead temporarily ponded on the soil surface. Once the solution had infiltrated and salt efflorescence were observed visually, an additional seven days were allowed for the salt crystals to form before harvesting by hand and dividing the soil into top and bottom depths. Salt efflorescence was easily harvested from all soil columns due to their high moisture content and low number of soil contact points. Salt and soil water contents were determined after harvesting salt efflorescence. In addition, a subset of extracted salts was tested for $NO_3$, P, K, Cl, Ca, Mg, Na, Zn, Fe, Mn, and Cu concentrations using an atomic absorption spectrophotometer (Model 210VGP, Buck Scientific) to determine their chemical composition. Approximately 5 g of the salt efflorescence from each sample was added to DI water to make the dilute salt solution for analysis. Salt solutions were also analyzed for total nitrogen and total organic carbon (TOC) using a TOC analyzer (Shimadzu TOC-VCPH Kyoto, Japan).

### *Experiment II - Sequential Harvesting*

The ability to repeatedly replenish the evaporative flux, and therefore re-initiate upward salt migration to the soil surface and obtain additional salt efflorescence for harvesting were evaluated over 28 days using the T1 application method and 0.01 M crystallization inhibitor concentration. Optimal conditions were chosen based on cores with highest observed salt extraction rates and $EC_e$ reductions as seen in Experiment I. Twenty-four soil columns [eight columns per soil texture, six columns per week (i.e., sandy loam, loam, and silty clay)] were subject to repeated infiltration of water to replenish the evaporative flux and sequential harvesting of salt efflorescence. All soil columns initially received the salt-saturated solution, crystallization inhibitor, and aqueous ammonia treatment. After seven days of salt efflorescence, the salt formations were harvested from all soil columns. The first group of designated cores (two soil columns from each soil texture) were then taken apart and separated into 0-3 and 3-6 cm depths. A 35 mL application of DI water was applied to the surface of the 18 remaining soil columns to induce capillary rise and initiate further salt efflorescence at the surface. After another seven days of salt efflorescence, new salt formations (if any) were harvested, the designated group of columns for week two were taken apart and separated into 0-3 and 3-6 cm depths, and another 35 mL of DI applied to the remaining 12 soil columns. This process was repeated until all soil column groups were taken apart and soil depths separated for chemical analyses. The repeated harvest of precipitated salts and the re-application of DI water ranged from one to three times for each set of columns.

In general, substantially less salt formations occurred after the initial harvesting of salt efflorescence even though water was applied repeatedly. Therefore, eight soil columns (two reps per week) were prepared with the loam soil (i.e., the soil texture yielding the largest quantities of salts in the previous soil columns) and the experiment repeated with a 35 mL solution of 0.01 M crystallization inhibitor and aqueous ammonia (5 mL) was repeatedly surface applied instead of DI water after the harvesting of salt efflorescence. Salt and soil water contents were determined for each soil depth as done in the previous experiments.

### ***Experiment III – Effect of Salt Species***

To determine if salt efflorescence would occur for different salt species similar to that of NaCl treated columns in experiments I and II, 18 soil columns were prepared using all three soil textures and 110 mL of $Na_2SO_4$, $MgSO_4$, and $CaSO_4$ saturated salt solutions (salt species common in naturally-occurring saline soils; two soil columns per soil texture and salt species combination). Similar to experiment II, the columns were treated with the 0.01 M concentration of the crystallization inhibitor using the T1 application method. After seven days of salt crystallization, salt efflorescence was harvested by hand, soil depths dissected, and water contents determined similarly to experiments I and II.

### ***Saturated Paste Extract EC, TDS and pH***

Saturated paste extracts from the 0-3 and 3-6 cm soil depths were prepared after harvesting salt efflorescence using the standard procedure described in Handbook 60 by adding together approximately 150 g of soil and various amounts of DI water (USDA, 1954). The pastes were stirred with a paint stirrer using a bench drill press and water was added until the desired consistency was obtained based on guidelines from Handbook 60 (USDA, 1954). Saturated pastes were allowed to rest for 18 h to reach a state of equilibrium before extracting the pore water with filter paper (Grade 413; VWR, Radnor, PA, USA) and a Buchner funnel under a vacuum. The EC of the saturated paste extracts ($EC_e$) were measured with a Sension 378 conductivity probe (Hach Co., Loveland, CO, USA). The maximum range of the conductivity meter was 199.9 dS $m^{-1}$. The $EC_e$ for some extracts exceeded 200 dS $m^{-1}$ and were therefore estimated from total dissolved solids (TDS) using quadratic conversion equations (see Appendix equations D1 and D2). The equation developed to convert from TDS to $EC_e$ was calibrated (n=63) and validated (n=63) for each experiment and salt type individually and was only used for soils with $EC_e$ values higher than 200 dS $m^{-1}$. For experiments I and II the RMSE and bias of the estimated $EC_e$ ranged from 5.01 to 6.54 and -1.69 to -0.52 dS $m^{-1}$, respectively. The TDS was determined from a 1 mL aliquot of the extract, weighing that wet weight, and then drying at 180°C for 1 h as described by the U.S Salinity Laboratory (Rhoades, 1996). Dry weight for each aliquot was measured and TDS calculated. The pH of the extracts was determined using an Accumet Basic 15 pH meter (Fisher Scientific, Pittsburgh, PA, USA).

### ***Statistical Analysis***

In experiment I, a mixed model analysis of variance (ANOVA) was used to determine the effects of crystallization inhibitor loading rate, application method, soil texture, and their interactions on the amount of harvestable salt efflorescence. The effects of crystallization inhibitor loading rate, application method, soil texture, soil depth and their interactions were evaluated on soil $EC_e$. In experiment II, a mixed model ANOVA was used to determine the effects of repeated water infiltrations on salt crystal growth and soil $EC_e$. Additionally, a mixed model ANOVA was used to determine the effects of applying the crystallization inhibitor on salt crystal growth and soil $EC_e$ to soil columns saturated with $Na_2SO_4$, $MgSO_4$, and $CaSO_4$ salt solutions. All analyses were done in SAS® with means separated using Tukeys at the 0.05 level (version 9.4, SAS Institute, Inc., Cary, NC).

## Results

### *Experiment I - Application Method, Soil Texture and Crystallization Inhibitor Concentration*

Experiment I aimed to evaluate a crystallization inhibitor used as a premixed, preventative method (T1) for NaCl-based brine spills and as a post-spill remediation method (T2 and T3). Soil columns amended with the crystallization inhibitor yielded 0 to 0.57 g $g^{-1}$ of the NaCl salts among all application methods, soil textures, and crystallization inhibitor concentrations (Table 5). Across all soils, $EC_e$ of the amended soil columns ranged from 129 to 268 dS $m^{-1}$ (Table 6).

The crystallization inhibitor concentration, application method, soil textures, and their interaction significantly affected salt extraction rates ($P < 0.0001$; Table 5). Overall, the crystallization inhibitor concentration used contributed to explaining 41% of the total variability among salt extraction in the mixed model ANOVA. Soil columns amended with 0.00001 and 0.0001M crystallization inhibitor concentrations yielded 0 and 0.02 g $g^{-1}$ of the applied NaCl, respectively, across the three application methods. However, incorporating the crystallization inhibitor (T3) resulted in zero salt extraction for all concentrations and soil textures (Table 5).

**Table 5.** Amount of salt extracted at different crystallization inhibitor concentrations using three application methods and three soil textures.

| Application Method | Concentration (mol/L) | Soil Texture |  |  | All Textures |
|---|---|---|---|---|---|
|  |  | Sandy Loam | Loam | Silty Clay |  |
|  |  | --------------------------------g $g^{-1}$ | -------------------------------- |  |  |
| T1[§] | 0.00001 | 0.00Ca[†‡] | 0.00Ba | 0.00Ca | 0.00B |
|  | 0.0001 | 0.01Cb | 0.00Bb | 0.15Ba | 0.05B |
|  | 0.001 | 0.38Ba | 0.38Aa | 0.36Aa | 0.37A |
|  | 0.01 | 0.48Aa | 0.47Aa | 0.37Ab | 0.44A |
|  | All Conc. | 0.22a | 0.21a | 0.22a |  |
| T2 | 0.00001 | 0.00Ba | 0.00Ca | 0.00Ba | 0.00C |
|  | 0.0001 | 0.00Ba | 0.00Ca | 0.00Ba | 0.00C |
|  | 0.001 | 0.01Bb | 0.13Ba | 0.01Bb | 0.05C |
|  | 0.01 | 0.46Aa | 0.57Aa | 0.29Ab | 0.44A |
|  | All Conc. | 0.12b | 0.18a | 0.08c |  |
| T3 | 0.00001 | 0.00Aa | 0.00Aa | 0.00Aa | 0.00A |
|  | 0.0001 | 0.00Aa | 0.00Aa | 0.00Aa | 0.00A |
|  | 0.001 | 0.00Aa | 0.00Aa | 0.00Aa | 0.00A |
|  | 0.01 | 0.00Aa | 0.00Aa | 0.00Aa | 0.00A |
|  | All Conc. | 0.00a | 0.00a | 0.00a |  |

[†]= Different lowercase letters within rows indicate significant differences at the 0.05 level.

[‡]= Different uppercase letters within columns indicate significant differences at the 0.05 level.

[§]= T1 (Salt plus inhibitor agent surface applied) T2 (Salt then inhibitor agent surface applied) T3 (Salt plus inhibitor agent incorporated)

**Table 6.** Soil $EC_e$ of soil columns treated with various crystallization inhibitor concentrations using three application methods in Experiment I.

| Application Method | Concentration (mol/L) | Soil Texture | | | All Textures |
|---|---|---|---|---|---|
| | | Sandy Loam | Loam | Silty Clay | |
| | | ----------------------------dS $m^{-1}$ | ---------------------------- | | |
| T1[§] | 0.00001 | 249Aa[†‡] | 261Aa | 192Ab | 224A |
| | 0.0001 | 257Aa | 259Aa | 169Ab | 216A |
| | 0.001 | 171Ba | 201Ba | 129Bb | 171B |
| | 0.01 | 160Ba | 170Ca | 140Bb | 157B |
| | All Conc. | 213a | 223a | 157b | |
| T2 | 0.00001 | 252Aa | 253Aa | 183Ab | 218A |
| | 0.0001 | 255Aa | 260Aa | 190Ab | 222A |
| | 0.001 | 259Aa | 217Bb | 186Ac | 214A |
| | 0.01 | 160Ba | 158Ca | 149Ba | 155B |
| | All Conc. | 218a | 213a | 177b | |
| T3 | 0.00001 | 256Aa | 268Aa | 185Ab | 223A |
| | 0.0001 | 250Aa | 256Aa | 192Ab | 223A |
| | 0.001 | 242Aa | 249Aa | 193Ab | 225A |
| | 0.01 | 242Aa | 244Aa | 183Ab | 219A |
| | All Conc. | 247a | 254a | 188b | |

[†] = Different lowercase letters within rows indicate significant differences at the 0.05 level.

[‡] = Different uppercase letters within columns indicate significant differences at the 0.05 level.

[§] = T1 (Salt plus inhibitor agent surface applied) T2 (Salt then inhibitor agent surface applied) T3 (Salt plus inhibitor agent incorporated)

In contrast, the surface application of the crystallization inhibitor either as a pre-mixed preventative method (T1) or as a post-spill remediation method (T2) yielded significantly more ($P<0.0001$) salt efflorescence above the soil surface for the 0.001M and 0.01M crystallization inhibitor concentrations compared to the controls whereas the columns applied with 0.00001 and 0.0001M concentrations did not obtain salt extractions different from zero (Table 5). A 0.01M concentration of the crystallization inhibitor applied via the T2 post-spill remediation method yielded the highest quantity of harvestable salt efflorescence (0.57 g $g^{-1}$) for the loam soil texture.

Salt extraction significantly differed among soil textures and crystallization inhibitor concentrations (Table 5). The silty clay soil yielded the lowest amount of extractable salt across all crystallization inhibitor concentrations for the T2 application method, with similar extraction rates observed across all soil textures for the T1 application method. The loam and sandy loam soils produced similar salt extraction rates of 0.57 and 0.46 g $g^{-1}$, respectively, for the T2 application method and extraction rates of 0.47 and 0.48 g $g^{-1}$, respectively, for the T1 application method.

Across all application methods, crystallization inhibitor concentrations and soil textures, mean soil $EC_e$ and pH values ranged from 129 to 268 dS $m^{-1}$, and 2.79 to 5.37, respectively (Table 6; see appendix Table C5). Mean $EC_e$ and pH values for different application methods at top and bottom core depths across all concentrations and soil textures ranged from 185 to 241 dS $m^{-1}$ and 3.45 to 4.61, respectively (Table 7; see appendix Table C7). Mean $EC_e$ and pH values for different soil textures at top and bottom core depths across all concentrations and application methods ranged from 97.6 to 169 dS $m^{-1}$ and 3.33 to 5.78, respectively (Table 7; see appendix Table C6). Average pH for the sandy loam, loam and silty clay textures without the addition of salts or a crystallization inhibitor were 4.9, 4.7 and 7.6, respectively. During analysis, the average measured pH for control soil columns that only received a 6 M NaCl solution was 3.11±0.56. Average pH across all soil textures and crystallization inhibitor concentrations for experimental columns that received the crystallization inhibitor, ammonia and 6 M NaCl solution was 3.89±0.83. In general, the highest average pH was observed in experimental columns using the highest inhibitor concentration (0.01 M; see appendix Table C5). Of the three textures used, the silty clay saw the largest reduction in pH, whereas pH reduction was negligible for the sandy loam and loam.

**Table 7.** Soil $EC_e$ by depth in columns treated with different crystallization inhibitor concentrations using three application methods and three soil textures in Experiment I.

| Chemical Property | Soil Depth | Application Method | | | All App. Methods |
|---|---|---|---|---|---|
| | | T1[§] | T2 | T3 | |
| | (cm) | ---------------------------$dS\ m^{-1}$--------------------------- | | | |
| $EC_e$[ǂ] | 0-3 | 211Ac[†‡] | 231Ab | 241Aa | 228A |
| | 3-6 | 185Bb | 189Bb | 218Ba | 197B |
| | All Depths | 198c | 210b | 230a | |

| Chemical Property | Soil Depth | Soil Texture | | | All Textures |
|---|---|---|---|---|---|
| | | Sandy Loam | Loam | Silty Clay | |
| | (cm) | ------------------------------$dS\ m^{-1}$------------------------------ | | | |
| $EC_e$ | 0-3 | 153Aa[†‡] | 156Aa | 169Aa | 159A |
| | 3-6 | 132Ba | 99.5Bb | 97.6Bb | 110B |
| | All Depths | 143a | 128a | 133a | |

[ǂ]= Electrical conductivity using saturated paste extract values.
[†]= Different lowercase letters within rows indicate significant differences at the 0.05 level.
[‡]= Different uppercase letters within columns indicate significant differences at the 0.05 level.
[§]= T1 (Salt plus inhibitor agent surface applied) T2 (Salt then inhibitor agent surface applied) T3 (Salt plus inhibitor agent incorporated)

A subset of salt extraction samples from experiment I (n=6) were added to DI water and tested for $NO_3$, P, K, Cl, Ca, Mg, Na, Zn, Fe, Mn, and Cu concentrations, total organic carbon and total nitrogen. Average ion concentrations for the samples were 0, 0, 1, 318, 8, 2, 512, 0, 1, 0 and 0 ppm, respectively. Total organic carbon and total nitrogen for the samples ranged from 1 to 4 and 8 to 9 ppm, respectively. Based on these results, the chemical composition of the extracted salts was confirmed to be > 97% composed of Na and Cl ions.

### *Experiment II - Sequential Salt Harvesting via Rehydration*

In experiment II, salt extraction rates did not differ from zero for all soil textures following the first week of harvest ($P \geq 0.05$; Table 8). Therefore, sequential salt extraction following initial salt harvest cannot be obtained by only rehydrating the soil with water. Additionally, salt extraction was negligible after week 1 when rehydrating the soil with

**Table 8.** Salt extraction following weekly DI $H_2O$ re-application in soil columns using a 0.01M crystallization inhibitor concentration and T1 application method for three soils.

| | Soil Texture | | | |
|---|---|---|---|---|
| | Sandy Loam | Loam | Silty Clay | All Textures |
| Week | ----------------------------------- | g $g^{-1}$ | ----------------------------------- | |
| 1 | 0.58Aa[†‡] | 0.56Aa | 0.27Ab | 0.47A |
| 2 | 0.03Ba | 0.05Ba | 0.01Bab | 0.03B |
| 3 | 0.01Ba | 0.01Ba | 0.00Ba | 0.01BC |
| 4 | 0.05Ba | 0.01Ba | 0.00Ba | 0.02B |
| All Weeks | 0.17a | 0.16a | 0.07b | |

[†]= Different lowercase letters within rows indicate significant differences at the 0.05 level.

[‡]= Different uppercase letters within columns indicate significant differences at the 0.05level.

additional amounts of DI water, crystallization inhibitor and ammonia. Soil $EC_e$ and pH values in the top and bottom soil depths of the columns ranged from 102 to 169 dS $m^{-1}$ and 3.83 to 4.91, respectively, among all three soils and week of sequential harvest. Similar to the amount of salt harvested, soils did not significantly decrease in $EC_e$ for the top and bottom depths following week 1.

### *Experiment III - Sulfate Salts*

Salt extraction rates were 0.03 and 0.03 g $g^{-1}$ for the control columns and columns treated with the crystallization inhibitor, respectively, across all three soils and all three sulfate salt types (see appendix Table C. Salt extraction rates did not differ among the control columns and columns treated with the crystallization inhibitor ($P = 0.92$). Overall, the largest amount of salt was extracted using the $NaSO_4$ salt and loam soil texture. Furthermore, the type of salt used had the largest influence on salt extraction percentages based on percent effect values. Average soil $EC_e$ and pH values across all depths and soil and sulfate-based salt types ranged from 1.96 to 63.1 dS $m^{-1}$ and 4.20 to 7.28, respectively. Average soil $EC_e$ and pH values for different sulfate-based salt types at top and bottom depths across all soil textures ranged from to 7.55 to 48.5 dS $m^{-1}$ and 4.02 to 7.11, respectively. The type of sulfate-based salt had the largest effect on differences in $EC_e$ and pH values for both control soil columns and columns amended with the crystallization inhibitor across all soil textures.

## Discussion

### *Crystallization Inhibitors in Ridged and Soft Porous Media*

Crystallization inhibitors are known to promote the formation of nondestructive efflorescence rather than destructive subflorescence (NaCl nucleation and crystallization inside the stone) in porous media such as building materials and industrial infrastructures (Gupta et al., 2012; Selwitz and Doehne, 2002; Franceschini et al., 2015). The efflorescence occurs as dendritic crystal growths with a low number of contact points on the surface of a porous media, whereas subflorescence occurs as massive cubic crystals, forming a hard crust within the media's pores (Selwitz and Doehne, 2002). By preventing pore blockage, the convective flux of water and solutes maintain at higher rates in porous media undergoing efflorescence and thus yield large amounts of salt efflorescence in a short period. The crystallization inhibitor limits pore blockage by enhancing super saturation, altering salt crystal morphology, and maintaining high evaporation rates near the media's surface (Veran-Tissoires et al., 2012; Lubelli et al., 2010; Selwitz and Doehne, 2002). This efflorescence of salts allows for easy harvesting without mechanically disturbing soft porous media such as soil.

Previous studies have hypothesized the underlying mechanisms and role of crystallization inhibitors in preventing salts from caking and crystallizing, although no clear consensus is seen throughout the literature. Glasner and Zidon (1974) showed that ferrocyanide ions have the same shape and structure of sodium chloride (NaCl) clusters and hypothesized that ferrocyanide could act as a nucleation site for NaCl. Geertman (2005) proposed that ferrocyanide ions adsorb onto the surface of NaCl, blocking crystal growth. Bode et al. (2012) adds to this, showing how ferrocyanide ions adsorb onto the face of sodium chloride crystals, replacing sodium and chloride ions. Due to this change within the crystal lattice, NaCl crystallization and caking is effectively prevented.

The current study presented here extends the potential use of crystallization inhibitors to the remediation of brine-contaminated soil. Sodium and potassium hexacyanoferrate have been used as crystallization inhibitors in studies focused on salt efflorescence in stones (Gupta et al., 2014; Gupta et al., 2012; Lubelli et al., 2010; Rivas et al., 2010; Lubelli and van Hees, 2007; Rodriguez-Navarro et al., 2002; Selwitz and Doehne, 2002). Gupta et al. (2012) performed drying experiments on slabs of fired clay brick and limestone to test the effectiveness of crystallization inhibitors to prevent salt weathering and the destruction of important cultural monuments and buildings. When they saturated these stones with a 3 M salt solution without a crystallization inhibitor, salt formations due to efflorescence on the fired clay brick and limestone were 0.07% and 0.1 g $g^{-1}$, respectively (Gupta et al., 2012). Salt efflorescence increased to 0.47 and 0.51 g $g^{-1}$ on the fired clay brick when 0.001 and 0.01M concentrations of a crystallization inhibitor were applied with the salt solution, respectively. Similarly, salt efflorescence increased to 0.36 and 0.69 g $g^{-1}$ on the limestone when 0.001 and 0.01M concentrations of a crystallization inhibitor were applied with the salt solution, respectively. We observed similar amounts of salt efflorescence (0.36 to 0.48 g $g^{-1}$) after infiltrating a NaCl solution with 0.001 and 0.01M concentration of the crystallization inhibitor ferric hexacyanoferrate on sandy loam, loam, and silty clay soil columns (Table 5).

Crystallization inhibitors have also been mixed or incorporated into building materials as a precautionary method to avoid structural damage from salts. Lubelli et al. (2010) used a sodium hexacyanoferrate crystallization inhibitor with NaCl mixed into the binder of a lime-cement mortar and observed salt efflorescence on the surface during subsequent drying. However, in our first experiment we did not observe salt efflorescence on soil columns with the crystallization inhibitor mechanically incorporated into the soil (i.e., T3; Table 5). This is likely due to the use of low crystallization inhibitor concentrations; salt efflorescence may have occurred if higher concentrations were applied to the soil.

These previously discussed studies did not evaluate the use of crystallization inhibitors in porous media where salts already crystallized and blocked pores. Rodriguez-Navarro and Ruiz-Agudo (2004) attempted to use a crystallization inhibitor on stones with salt already crystallized in the media's pores. They observed no effect of the crystallization inhibitor to promote salt efflorescence on the stone's surface. In contrast, we observed the largest quantities of salt efflorescence (up to 0.57 $g\ g^{-1}$) in soil columns when salts already precipitated as a cemented crust prior to infiltrating a crystallization inhibitor suspension (i.e., T2; Table 5).

Cassar et al. (2008) observed a crystallization inhibitor's ability to inhibit pore blockage and promote the formation of dendrite salt formations for salt solutions other than NaCl. They observed 0.47 $g\ g^{-1}$ of $NaSO_4$ in a saturated limestone slab effloresced on the surface when using a phosphorylated crystallization inhibitor. Naturally occurring salinity at land surfaces around the world often occurs as sulfate-based salinity. These salts contribute to some of the largest limitations for agricultural crop production. However, the crystallization inhibitor ferric hexacyanoferrate used in our study did not produce significant quantities of salt efflorescence in experiment III when sulfate-based salts were used. However, further research should include the evaluation of other crystallization inhibitors, such as phosphorylated compounds, for alleviating sulfate-based soil salinity (Cassar et al., 2008; Rodriguez-Navarro et al., 2002).

### *Crystallization Inhibitor Limitations, Toxicity, and Engineered Materials for Brine Spill Remediation*

Obtaining significant salt extraction rates with a crystallization inhibitor is dependent on its degradation rate. In preliminary experiments, we used oxalic acid to solvate the ferric hexacyanoferrate (a kinetically inert, iron cyanide mineral) to the reaction products Fe and hexacyanoferrate (the compound that inhibits salt crystallization; Meeussen et al., 1992; Sharpe, 1976). However, the hexacyanoferrate degradation half-life can be rapid in solutions of pH < 4 or when exposed to ultra violet light, producing the reaction products of free cyanide and hydrogen cyanide; half-life of hexacyanoferrate in solutions of pH 4 to 7 increases from 1 to 1,000 years (Meeussen et al., 1992). The suspension of ferric hexacyanoferrate in oxalic acid did not produce salt efflorescence at the surface of soil columns; likely due to the degradation of the crystallization inhibitor hexacyanoferrate. Therefore, mixing compounds with the crystallization inhibitor hexacyanoferrate (i.e., sodium hexacyanoferrate, potassium hexacyanoferrate, or ferric hexacyanoferrate) with acids are not expected to produce salt efflorescence and will likely release toxic reaction products of free cyanide and hydrogen cyanide. We recommend using aqueous ammonia to solvate compounds containing the crystallization inhibitor hexacyanoferrate as done in the current study. We chose ferric hexacyanoferrate as the crystallization inhibitor source in this study due to its extreme stability during handling and shipping and the long half-life of the crystallization inhibitor for a large range of soil pH (Meussen et al., 1992; Sharpe, 1976).

The use of hexacyanoferrate for remediating soils contaminated with brine can produce cyanide compounds. However, the potential for toxicity to humans and the environment is considered low due to the use of dilute suspensions and its application not being in small enclosures where the volatile cyanide reaction products can accumulate to toxic levels. Additionally, other crystallization inhibitors with low toxicity reaction products may produce similar salt extraction rates. Therefore, hexacyanoferrate is used here only as an example of a crystallization inhibitor for remediating brine spills (Daigh and Klaustermeier, 2016). The authors also acknowledge the potential to incorporate a crystallization inhibitor into mats or other structures during their fabrication similar to the mortar used by Lubelli et al. (2010). These fabricated materials could then be laid out onto the soil surface and allow salt efflorescence to occur if the materials maintained good contact with the soil surface. This approach would eliminate the need to infiltrate a crystallization inhibitor directly onto the soil surface, further minimizing the potential for toxic reaction products to harm the environment, and allow repeated use of the crystallization inhibitor to limit remediation costs.

The effect of crystallization inhibitors on soil pH has not been assessed in any previous literature. In our study it is not known why measured soil pH was lower in salt saturated columns and columns with the crystallization inhibitor applied compared to bulk soil. Land managers and environmental consultants should be aware of the potential effects of crystallization inhibitors on either acidic or basic soils, as crystallization inhibitors applied to acidic soils may induce aluminum toxicity, but may also reduce pH and potentially alleviate iron chlorosis in basic soils with high pH. The effects of lowering soil pH should be assessed at each particular contamination site before resuming agricultural and rangeland production. Further studies will aim to identify the cause of this pH reduction and assess the potential impact of crystallization inhibitors on soil chemical properties.

Relative humidity is also a factor that can alter the effectiveness of crystallization inhibitors to yield salt efflorescence. Gupta et al. (2014) observed crystallization inhibitors producing larger salt yields in fast drying, low humidity conditions. Therefore, local atmospheric moisture regimes may affect salt extraction rates across regions, producing varying results. Additionally, the potential for wind and water to transport effloresced salts to adjacent fields is unknown and needs to be evaluated in field conditions. Structures to divert wind (as well as vertical air pressure gradients from wind gusts) and water flows could reduce the likelihood of extracted salt losses. However, further research in field conditions is needed to evaluate these risks.

Based on results from this study, it is not feasible to simply rehydrate a salt-affected soil after initial crystallization inhibitor application and salt extraction to allow further salt efflorescence at the soil surface. In addition, salt extraction was negligible after reapplying the deionized water, crystallization inhibitor and ammonia solution after initial harvest. More research is needed to determine if crystallization inhibitors are only effective under salt saturated conditions and if salt extraction rates diminish as salt content decreases.

## Conclusions

The use of crystallization inhibitors appears to be feasible for remediating salt-contaminated soils and show potential for coupling with other remediation methods. Salts harvested using a crystallization inhibitor is a permanent and more effective form of desalinization of brine-affected sites as compared to leaching methods. Furthermore, crystallization inhibitors may be more suitable for long-term soil conservation efforts than ex-situ remediation methods such as topsoil excavation. This in-situ method allowed for average salt harvest as high as 0.46, 0.57 and 0.29 g $g^{-1}$ from NaCl contaminated sandy, sandy loam and silty clay soils, respectively, over a seven-day period. However, the crystallization inhibitor is not feasible to yield significant sulfate salt efflorescence at the concentrations used in this laboratory study. Other crystallization inhibitors may be useful in yielding harvestable sulfate-based salt efflorescence. Future studies will include the evaluation of crystallization inhibitors in field conditions and developing engineered soil mats fabricated with a crystallization inhibitor to replace the direct application of the compounds to the soil surface.

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# GENERAL CONCLUSIONS

The relationships between all EC methods were highly correlated ($r^2$=0.91 to 0.97, $P$ <0.0001), indicating strong evidence that $EC_e$ of soils contaminated with NaCl-dominated brine can be accurately estimated from $EC_{1:1}$ and $EC_{1:5}$ values using the newly developed conversion equations in this study. Furthermore, the $EC_{1:1}$ and $EC_{1:5}$ values for all equilibration time periods were within the RMSE for the predicted vs. measured $EC_e$, indicating that accurate measurements of $EC_{1:1}$ and $EC_{1:5}$ can be obtained immediately after 10 s of mixing.

The use of crystallization inhibitors appears to be feasible for remediating salt-contaminated soils and could be used in place of or in combination with other remediation methods. Using this in-situ method allowed an average of 0.46, 0.57 and 0.29 g $g^{-1}$ of salts to be extracted from NaCl-contaminated sandy loam, loam and silty clay soils, respectively, over a period of seven days for some combinations of the different crystallization inhibitor concentrations and application methods. More research is needed to determine whether salt extraction after initial inhibitor application and salt removal is limited due to a decrease in inhibitor concentration or from a decrease in soluble salt amounts. Additional research is also needed to determine the efficacy of crystallization inhibitors in field conditions. The new data and inferences from this research thesis on EC conversion equations and alternative forms of brine spill remediation will allow environmental consultants, remediation specialists, and research scientists to assess and reduce the salinity of brine-contaminated soils in a more efficient manner than previously known.

# APPENDIX A. CLEAN WATER LEACHING USING HYDRUS 1-D

We used HYDUS-1D to simulate time estimates for solute and water movement through a homogenous soil profile. This simulation is only used as an example and the model was not calibrated or validated with actual soil columns; the original source code was used as is with the UNSATCH subroutines. A silt loam textured soil (Beotia Soil Series) was simulated with model parameters for the water retention and hydraulic conductivity curves [i.e., Mualem (1976) and van Genuchten (1980) models] estimated with the ROSETTE neural network hierarchal pedotransfer functions. Soil bulk density was set to 1.3 g $cm^{-3}$ with a porosity of 50.9% assuming a particle density of 2.65 g $cm^{-3}$. When simulating a 150 cm deep soil profile, a 76.4 cm depth of water is equivalent to one pore volume.

We initially simulated 100 years of constant ponding of fresh water at the soil surface with initial soil water potentials set at 0 cm $H_2O$ at the soil surface and -100 cm $H_2O$ at all other soil depths (i.e., Dirichlet boundary). Initial water movement throughout the soil profile was rapid during the first day of simulation. Approximately 2 cm of water infiltrated during the first day. Afterwards, water movement slowed substantially to only 0.7cm of infiltration every 10,000 days due to the amount of sodium in the soil. This suggests a timeline of approximately 2,990 years to drain 76.4 cm of water, or one pore volume, through the 150 cm deep soil profile. We then run to simulation out to 3000 years which estimated a timeline of 2,500 years to drain one pore volume of fresh water from the 150 cm soil profile.

## APPENDIX B. EM-38 3-D MAP IMAGERY FOR CHAPTER I STUDY SITES

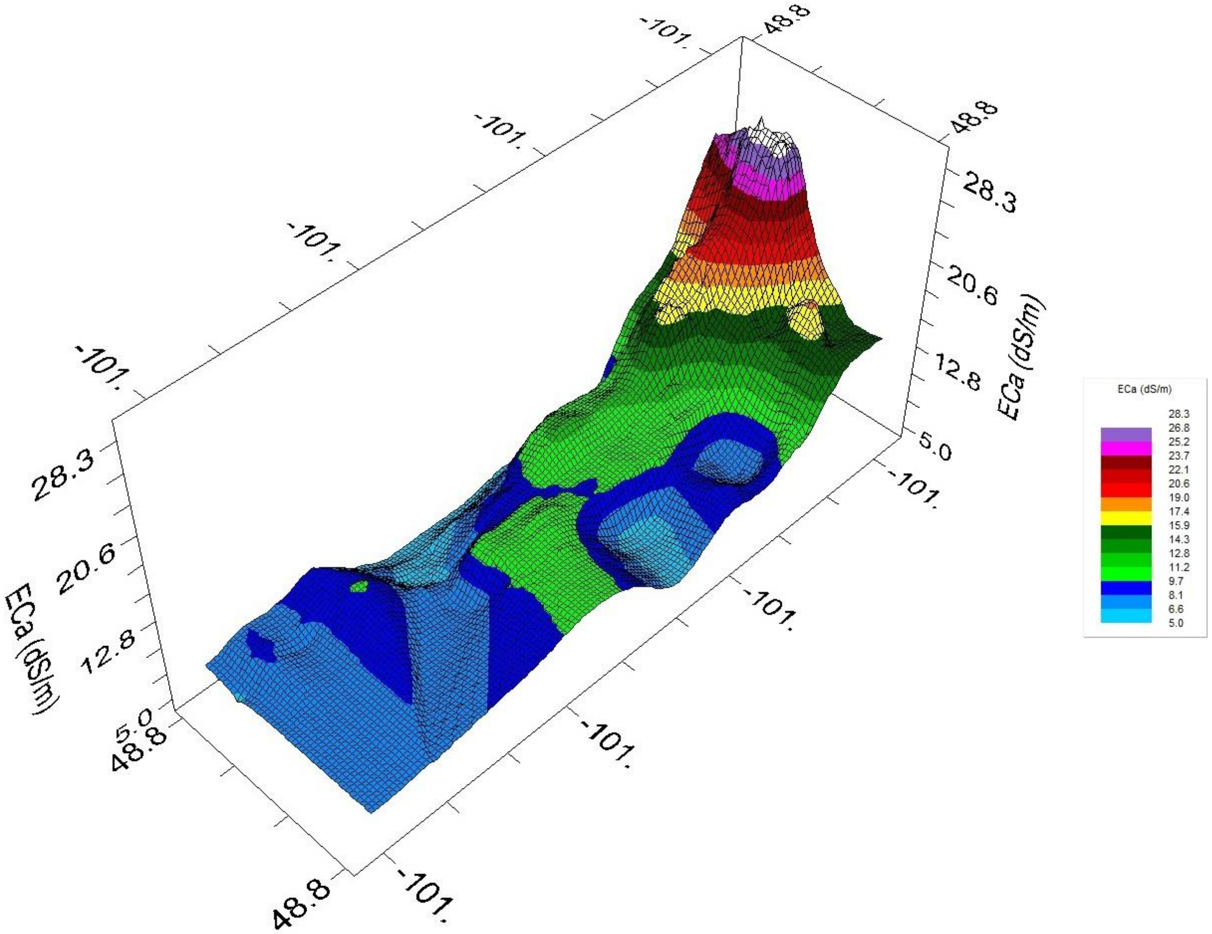

**Figure B1.** Electromagnetic (EM-38) soil salinity mapping imagery for study site one.

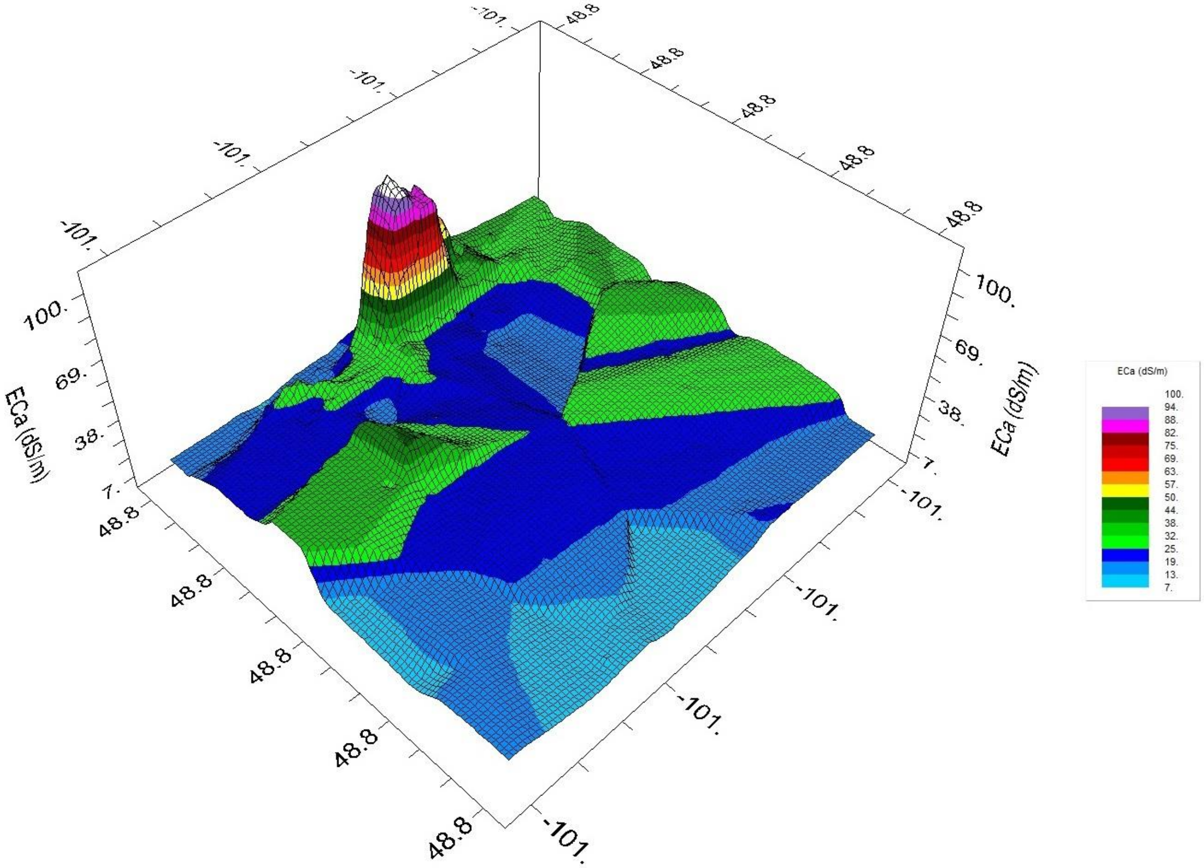

**Figure B2.** Electromagnetic (EM-38) soil salinity mapping imagery for study site two.

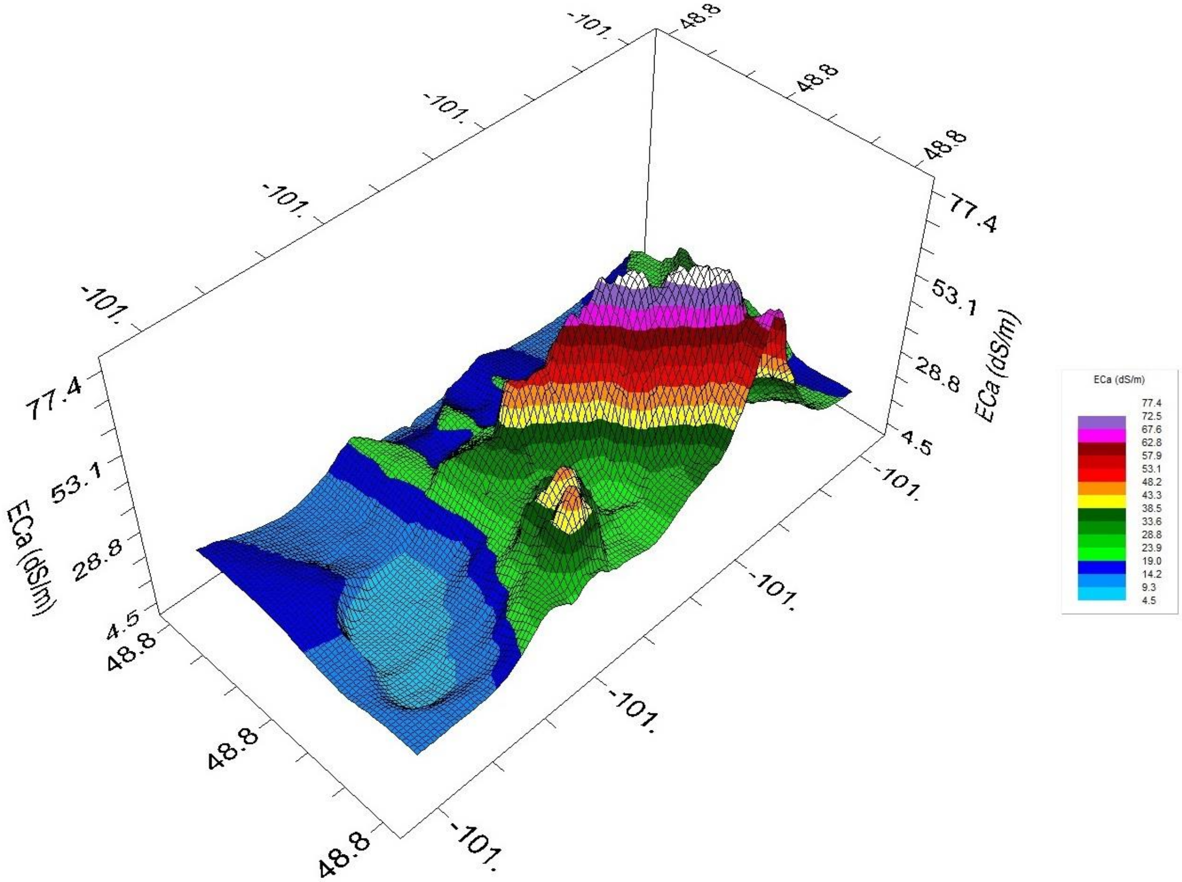

**Figure B3.** Electromagnetic (EM-38) soil salinity mapping imagery for study site three.

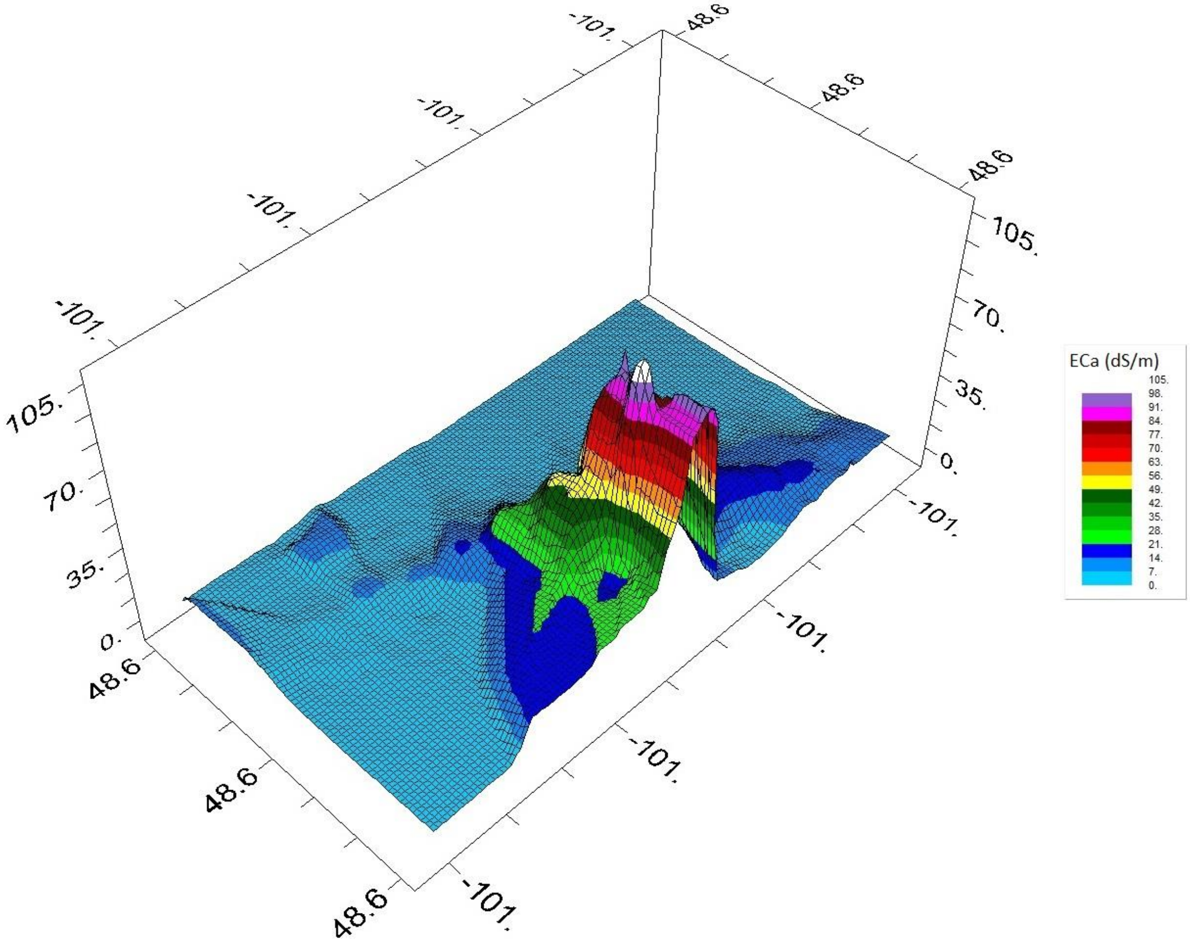

**Figure B4.** Electromagnetic (EM-38) soil salinity mapping imagery for study site four.

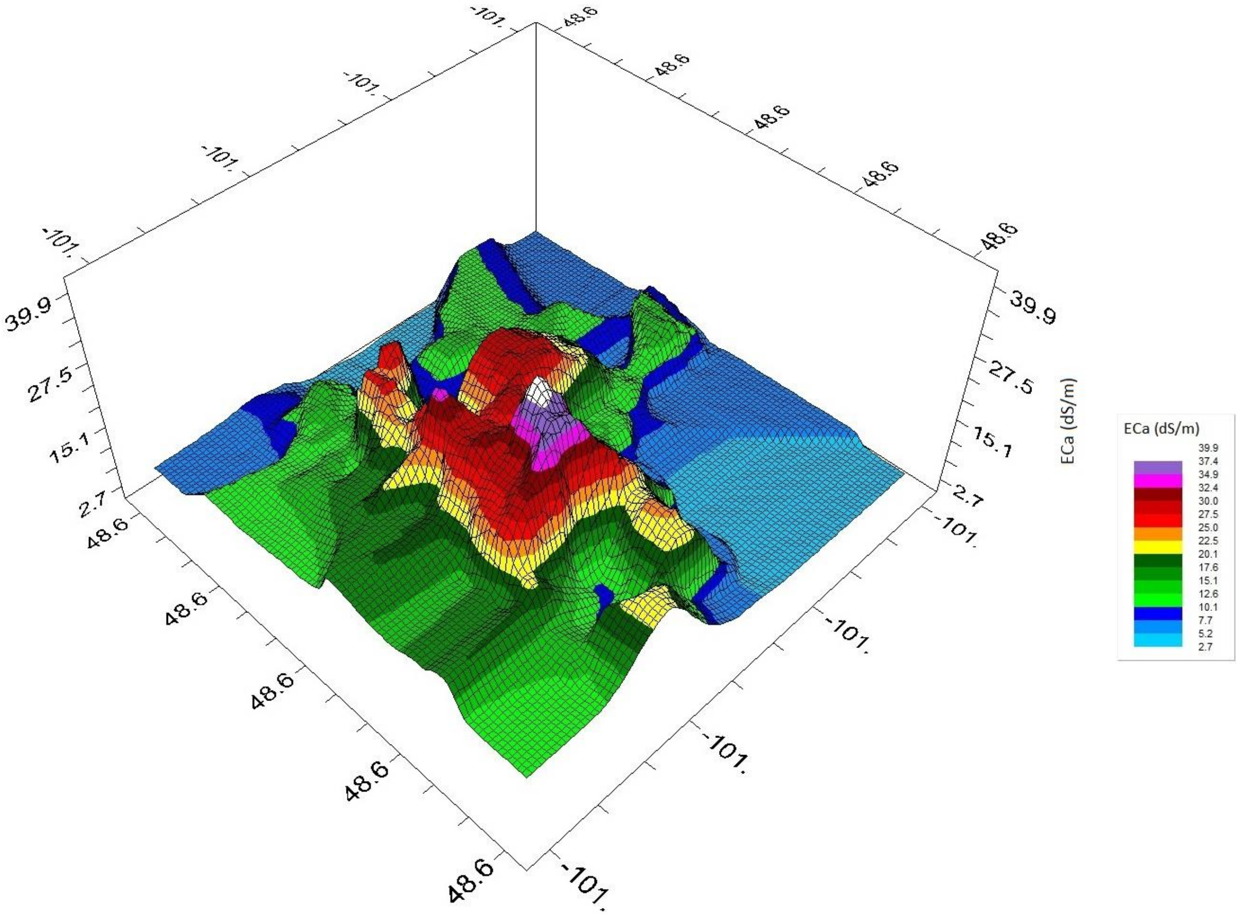

**Figure B5.** Electromagnetic (EM-38) soil salinity mapping imagery for study site five.

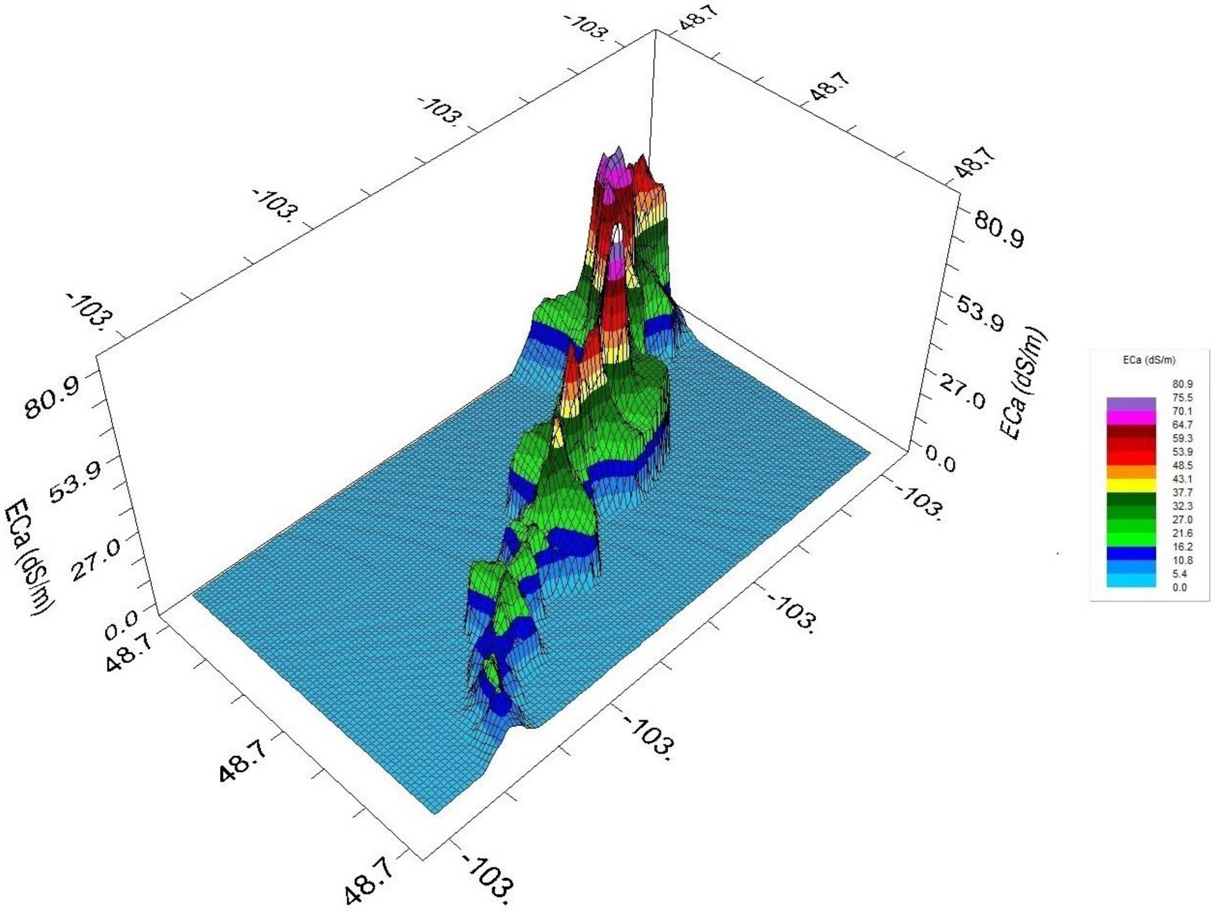

**Figure B6.** Electromagnetic (EM-38) soil salinity mapping imagery for study site six.

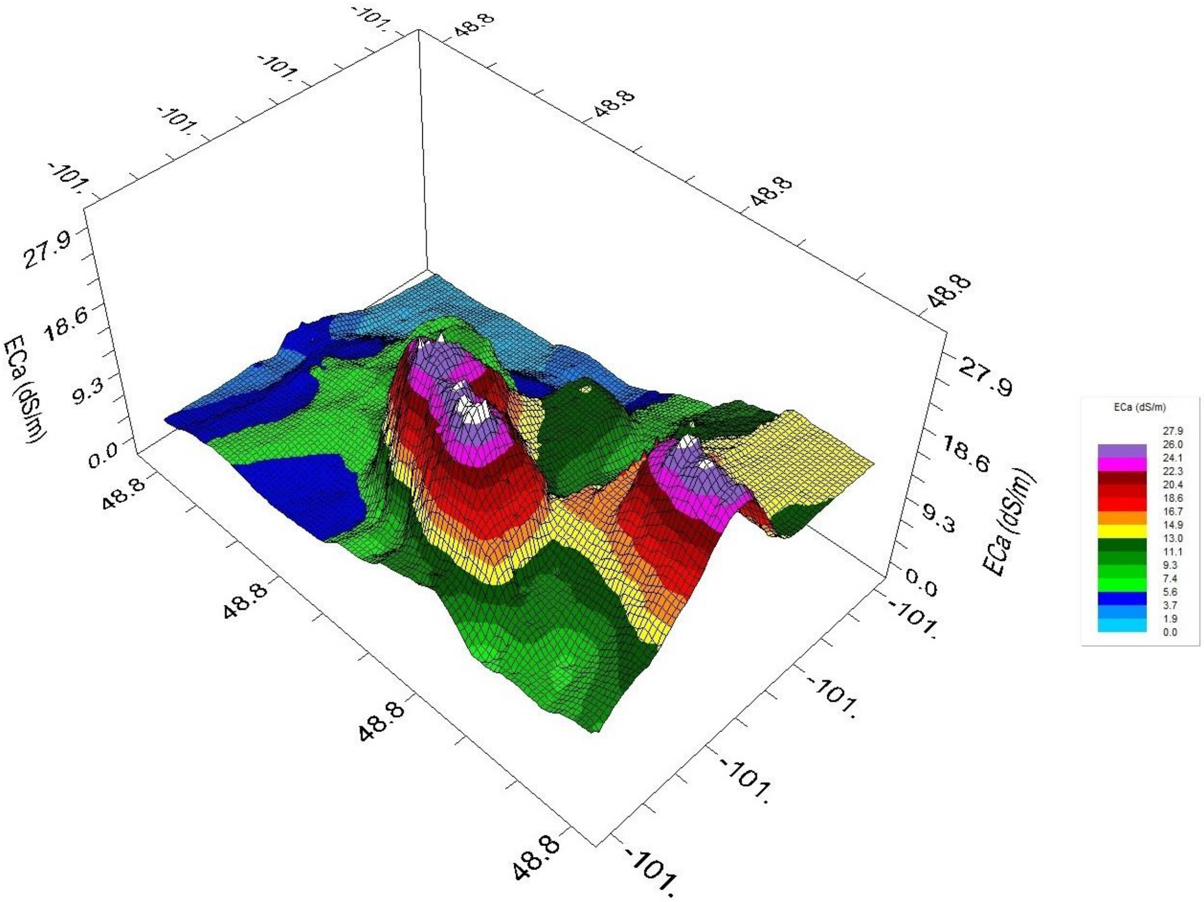

**Figure B7.** Electromagnetic (EM-38) soil salinity mapping imagery for study site seven.

# APPENDIX C. ADDITIONAL CHAPTER II TABLES AND FIGURES

**Table C1.** Soil chemical properties for all soil textures, application methods and crystallization inhibitor concentrations used in experiment I.

| | Salt Water Content | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Sandy Loam | | | Loam | | | Silty Clay | | |
| | T1[§] | T2 | T3 | T1 | T2 | T3 | T1 | T2 | T3 |
| Conc.[†] | ---------------------------------- | | | | % | | | | ---------------------------------- |
| Control | -[‡] | - | - | - | - | - | - | - | - |
| 0.01 | 54.4 | 50.7 | - | 54.3 | 34.3 | - | 16.1 | 17.0 | - |
| 0.001 | 54.7 | | - | 52.8 | - | - | 3.00 | - | - |
| 0.0001 | - | - | - | - | - | - | 12.6 | - | - |
| 0.00001 | - | - | - | - | - | - | - | - | - |

| | Soil Water Content | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Sandy Loam | | | Loam | | | Silty Clay | | |
| | T1 | T2 | T3 | T1 | T2 | T3 | T1 | T2 | T3 |
| Conc.[†] | ---------------------------------- | | | | % | | | | ---------------------------------- |
| Control | | 18.1 | | | 18.8 | | | 21.5 | |
| 0.01 | 13.4 | 13.4 | 20.9 | 13.1 | 11.4 | 20.9 | 19.9 | 20.8 | 24.4 |
| 0.001 | 14.6 | 20.6 | 21.2 | 15.0 | 19.4 | 20.4 | 19.7 | 23.8 | 25.1 |
| 0.0001 | 20.6 | 20.2 | 20.8 | 19.2 | 19.4 | 20.8 | 22.8 | 24.2 | 25.0 |
| 0.00001 | 20.3 | 21.7 | 20.9 | 19.5 | 21.6 | 19.8 | 25.1 | 24.2 | 24.6 |

[§]= T1 (Salt plus inhibitor agent surface applied) T2 (Salt then inhibitor agent surface applied) T3 (Salt plus inhibitor agent incorporated)

[†]= Concentration of crystallization inhibitor used

[‡]= Dashed columns indicate non-observable data due to negligible quantities (<5 g) of salt extracted

**Table C2.** Soil and salt water content for all weeks and soil textures used in experiment II.

| | Salt Water Content | | | Soil Water Content | | |
|---|---|---|---|---|---|---|
| Week | Sandy Loam | Loam | Silty Clay | Sandy Loam | Loam | Silty Clay |
| | ---------------% | | --------------- | ---------------% | | --------------- |
| Cntl | - | - | - | 18.1 | 18.8 | 21.5 |
| 1 | 38.8 | 43.1 | 16.1 | 19.7 | 19.3 | 19.9 |
| 2 | -[†] | - | - | 19.6 | 19.8 | 19.6 |
| 3 | - | - | - | 20.5 | 20.5 | 20.8 |
| 4 | - | - | - | 19.3 | 19.8 | 19.9 |

[†]= Dashed columns indicate non-observable data due to negligible quantities (<5 g) of salt extracted.

**Table C3.** Soil and salt water content for all soil textures and salt types used in experiment III.

| | Salt Water Content | | | Soil Water Content | | |
|---|---|---|---|---|---|---|
| Salt Type | Sandy Loam | Loam | Silty Clay | Sandy Loam | Loam | Silty Clay |
| | ---------------%--------------- | | | ---------------%--------------- | | |
| Cntl-NaSO$_4$[†] | -[‡] | - | 20.4 | 14.4 | 14.2 | 19.2 |
| Cntl-MgSO$_4$ | - | - | - | 17.3 | 18.9 | 19.9 |
| Cntl-CaSO$_4$ | - | - | - | 9.71 | 9.24 | 18.2 |
| NaSO$_4$ | 8.00 | 13.4 | 5.67 | 17.2 | 17.6 | 22.8 |
| MgSO$_4$ | 33.1 | - | 25.2 | 20.5 | 20.1 | 22.6 |
| CaSO$_4$ | - | - | - | 12.3 | 10.9 | 20.9 |

[†]= Control (Cntl) columns received salt without the addition of a crystallization inhibitor

[‡]= Dashed columns indicate non-observable data due to negligible quantities (<5 g) of salt extracted.

**Table C4.** Soil TDS of soil columns treated with various crystallization inhibitor concentrations using three application methods in Experiment I.

| Application Method | Concentration (mol/L) | Soil Texture | | | |
|---|---|---|---|---|---|
| | | Sandy | Loam | Silty Clay | All Soils |
| | | -----------------------------g l$^{-1}$----------------------------- | | | |
| T1[§] | 0.00001 | 212Aa[†‡] | 234Aa | 146Ab | 197A |
| | 0.0001 | 217Aa | 223Aa | 128Ab | 189A |
| | 0.001 | 146Ba | 157Ba | 92Bb | 132B |
| | 0.01 | 116Ca | 124Ca | 97Ba | 112C |
| | All Conc. [ǂ] | 173a | 184a | 116b | |
| T2 | 0.00001 | 213Ba | 217Aa | 157Ab | 196B |
| | 0.0001 | 231Aa | 230Aa | 153Ab | 205A |
| | 0.001 | 233Aa | 175Bb | 154Ac | 187C |
| | 0.01 | 113Ca | 115Ca | 116Ba | 115D |
| | All Conc. | 198a | 184b | 145c | |
| T3 | 0.00001 | 221Aa | 243Aa | 147Ab | 204A |
| | 0.0001 | 207Aa | 219Ba | 153Ab | 193A |
| | 0.001 | 206Aa | 217Ba | 150Ab | 191A |
| | 0.01 | 199Aa | 188Ca | 138Ab | 175B |
| | All Conc. | 208a | 217a | 147b | |

[§]= T1 (Salt plus inhibitor agent surface applied) T2 (Salt then inhibitor agent surface applied)
T3 (Salt plus inhibitor agent incorporated)

[†]= Different lowercase letters within rows indicate significant differences at the 0.05 level.

[‡]= Different uppercase letters within columns indicate significant differences at the 0.05 level.

[ǂ]= All concentrations

**Table C5.** Soil pH of soil columns treated with various crystallization inhibitor concentrations using three application methods in Experiment I.

| Application Method | Concentration (mol/L) | Soil Texture | | | |
|---|---|---|---|---|---|
| | | Sandy Loam | Loam | Silty Clay | All Textures |
| T1 | 0.00001 | 3.68Bb[†‡] | 3.30Bc | 4.59Ba | 3.86B |
| | 0.0001 | 3.55Bb | 3.16Bc | 4.77Ba | 3.82B |
| | 0.001 | 3.96Ab | 3.48Ac | 5.37Aa | 4.27A |
| | 0.01 | 3.95Ab | 3.63Ac | 5.17Aa | 4.25A |
| | All Conc.[ǂ] | 3.78b | 3.39c | 4.97a | |
| T2 | 0.00001 | 3.15Bb | 2.79Bc | 4.30Ba | 3.41C |
| | 0.0001 | 3.34Bb | 2.88Bc | 4.29Ba | 3.50C |
| | 0.001 | 3.29Bb | 3.29Ab | 4.35Ba | 3.64B |
| | 0.01 | 3.58Ab | 3.36Ab | 4.83Aa | 3.92A |
| | All Conc. | 3.34b | 3.08c | 4.44a | |
| T3 | 0.00001 | 3.72Ab | 3.25Ac | 4.77Aa | 3.91A |
| | 0.0001 | 3.53Ab | 3.28Ab | 5.12Aa | 3.98A |
| | 0.001 | 3.72Ab | 3.29Ac | 5.24Aa | 4.08A |
| | 0.01 | 3.80Ab | 3.50Ab | 5.07Aa | 4.12A |
| | All Conc. | 3.69b | 3.33c | 5.05a | |

[§]= T1 (Salt plus inhibitor agent surface applied) T2 (Salt then inhibitor agent surface applied) T3 (Salt plus inhibitor agent incorporated)

[†]= Different lowercase letters within rows indicate significant differences at the 0.05 level.

[‡]= Different uppercase letters within columns indicate significant differences at the 0.05 level.

[ǂ]= All concentrations

**Table C6.** Soil chemical properties by depth across all crystallization inhibitor concentrations for different soil textures used in Experiment I.

| | | Soil Texture | | | |
|---|---|---|---|---|---|
| | Depth | Sandy Loam | Loam | Silty Clay | All Textures |
| | cm | -------------------------------g l$^{-1}$------------------------------- | | | |
| TDS[ǂ] | 0-3 | 106Ab[†‡] | 114Aab | 127Aa | 116A |
| | 3-6 | 93Aa | 73Bb | 72Bb | 79B |
| | All Depths | 100a | 94a | 99a | |
| pH | 0-3 | 4.80Ab | 3.63Ac | 5.78Aa | 4.73A |
| | 3-6 | 3.55Bb | 3.33Bb | 5.24Ba | 4.04B |
| | All Depths | 5.51a | 3.48c | 4.17b | |

[ǂ]= Total dissolved solids

[†]= Different lowercase letters within rows indicate significant differences at the 0.05 level.

[‡]= Different uppercase letters within columns indicate significant differences at the 0.05 level.

**Table C7.** Soil chemical properties by depth in columns treated with different crystallization inhibitor concentrations using three application methods in Experiment I.

|  | Depth | Application Method |  |  | All Methods |
|---|---|---|---|---|---|
|  |  | T1§ | T2 | T3 |  |
|  | cm | ---------------------g l$^{-1}$--------------------- |  |  |  |
| TDSǂ | 0-3 | 169Ac†‡ | 197Ab | 208Aa | 192A |
|  | 3-6 | 146Bb | 154Bb | 173Ba | 158B |
|  | All Depths | 158c | 176b | 191a |  |
| pH | 0-3 | 4.61Aa | 3.79Ac | 4.13Ab | 4.18A |
|  | 3-6 | 3.49Bb | 3.45Bb | 3.92Ba | 3.62B |
|  | All Depths | 4.05a | 3.62b | 4.02a |  |

§= T1 (Salt plus inhibitor agent surface applied) T2 (Salt then inhibitor agent surface applied) T3 (Salt plus inhibitor agent incorporated)

ǂ= Total dissolved solids

†= Different lowercase letters within rows indicate significant differences at the 0.05 level.

‡= Different uppercase letters within columns indicate significant differences at the 0.05 level.

**Table C8.** Soil chemical properties for soil columns with salt growths harvested and rehydrated weekly, averaged across soil types in Experiment II.

|  |  | Week |  |  |  |  |
|---|---|---|---|---|---|---|
| Chemical Property | Depth | 1 | 2 | 3 | 4 | All Weeks |
|  | cm | ------------------------------dS m$^{-1}$------------------------------ |  |  |  |  |
| EC$_e$ | 0-3 | 169Aa†‡ | 160Aa | 153Aa | 155Aa | 159A |
|  | 3-6 | 119Ba | 108Ba | 110Ba | 102Ba | 110B |
|  | All Depths | 144a | 134ab | 131ab | 129b |  |
|  |  | -----------------------------g L$^{-1}$----------------------------- |  |  |  |  |
| TDS | 0-3 | 122Aa | 117Aa | 110Aa | 114Aa | 116A |
|  | 3-6 | 85.3Ba | 77.2Ba | 79.6Ba | 75.2Ba | 79.4B |
|  | All Depths | 104a | 96.9a | 94.9a | 94.4a |  |
| pH | 0-3 | 4.57Ab | 4.91Aa | 4.72Aab | 4.73Aab | 4.73A |
|  | 3-6 | 3.83Bbc | 3.90Bb | 4.26Ba | 4.17Bab | 4.04B |
|  | All Depths | 4.20a | 4.40ab | 4.49b | 4.45b |  |

§= Electrical conductivity of using saturated paste extract values.

†= Different lowercase letters within rows indicate significant differences at the 0.05 level.

‡= Different uppercase letters within columns indicate significant differences at the 0.05 level.

ǂ= Total dissolved solids

**Table C9.** Amount of salt extracted using control and experimental soil columns on three sulfate based salts in Experiment III.

| | Salt Type | | | |
|---|---|---|---|---|
| Core Type | $Na_2SO_4$ | $MgSO_4$ | $CaSO_4$ | All Salts |
| | ----------$g\ g^{-1}$---------- | | | |
| Control[§] | 0.09Aa[†‡] | 0.01Ab | 0.00Ab | 0.03A |
| Experimental | 0.09Aa | 0.02Ab | 0.00Ab | 0.03A |
| All Columns | 0.09a | 0.01b | 0.00b | |

[§]= Control columns received salt without the addition of a crystallization inhibitor

[†]= Different lowercase letters within rows indicate significant differences at the 0.05 level.

[‡]= Different uppercase letters within columns indicate significant differences at the 0.05 level.

**Table C10.** Soil chemical properties using different sulfate-based salts and different soil types in Experiment III

| | | Soil Texture | | | |
|---|---|---|---|---|---|
| Chemical Property | Salt Type | Sandy Loam | Loam | Silty Clay | All Soils |
| | | ----------$dS\ m^{-1}$---------- | | | |
| $EC_e$[§] | $NaSO_4$ | 60.9Aa[†‡] | 63.1Aa | 29.4Ab | 51.1A |
| | $MgSO_4$ | 44.1Ba | 50.9Ba | 21.2Bb | 38.7B |
| | $CaSO_4$ | 3.10Ca | 2.43Ca | 1.96Ca | 2.50C |
| | All Salts | 36.1a | 38.8a | 17.5b | |
| | | ----------$g\ l^{-1}$---------- | | | |
| TDS[ǂ] | $NaSO_4$ | 71.6Bb | 80.3Ba | 30.5Ac | 60.8B |
| | $MgSO_4$ | 105Ab | 123Aa | 37.7Ac | 88.5A |
| | $CaSO_4$ | 3.96Ca | 3.31Ca | 2.40Bb | 3.22C |
| | All Salts | 60.1b | 68.9a | 23.5c | |
| pH | $NaSO_4$ | 4.87Ab | 4.26Ac | 7.25Aa | 5.46A |
| | $MgSO_4$ | 4.49Bb | 4.20Ac | 6.68Ba | 5.13B |
| | $CaSO_4$ | 4.79Ab | 4.41Ac | 7.28Aa | 5.50A |
| | All Salts | 4.72b | 4.29c | 7.07a | |

[§]= Electrical conductivity of using saturated paste extract values.

[†]= Different lowercase letters within rows indicate significant differences at the 0.05 level.

[‡]= Different uppercase letters within columns indicate significant differences at the 0.05 level.

[ǂ]= Total dissolved solids

**Table C11.** Soil chemical properties for different soil types at different depths across salt types ($NaSO_4$, $MgSO_4$ and $CaSO_4$) in Experiment III

| Chemical Property | Depth | Soil Type<br>Sandy | Loam | Silty Clay | All Soils |
|---|---|---|---|---|---|
| | (cm) | -------------------------dS m$^{-1}$ | ------------------------- | | |
| | 0-3 | 42.5Ab[†‡] | 48.5Aa | 27.4Ac | 39.5A |
| $EC_e$[§] | 3-6 | 29.6Ba | 29.1Ba | 7.55Bb | 22.1B |
| | All Depths | 36.1a | 38.8a | 17.5b | |
| | | ----------------------------g l$^{-1}$ | ---------------------------- | | |
| | 0-3 | 76.1Ab | 88.0Aa | 38.3Ac | 67.5A |
| TDS[ǂ] | 3-6 | 44.2Ba | 49.7Ba | 8.81Bb | 34.2B |
| | All Depths | 60.1b | 68.9a | 2.35c | |
| | 0-3 | 5.29Ab | 4.56Ac | 7.03Aa | 5.62A |
| pH | 3-6 | 4.15Bb | 4.02Bb | 7.11Aa | 5.09B |
| | All Depths | 4.71b | 4.29c | 7.07a | |

[§]= Electrical conductivity of using saturated paste extract values.

[†]= Different lowercase letters within rows indicate significant differences at the 0.05 level.

[‡]= Different uppercase letters within columns indicate significant differences at the 0.05 level.

[ǂ]= Total dissolved solids

**Table C12.** Soil chemical properties at different depths when using different sulfate-based salts in Experiment III

| Chemical Property | Depth | Salt Type<br>$Na_2SO_4$ | $MgSO_4$ | $CaSO_4$ | All Salts |
|---|---|---|---|---|---|
| | (cm) | -------------------------dS m$^{-1}$ | ----------------------- | | |
| | 0-3 | 68.1Aa[†‡] | 47.0Ab | 3.37Ac | 39.5A |
| $EC_e$[§] | 3-6 | 34.2Ba | 30.5Ba | 1.62Bb | 22.1B |
| | All Depths | 51.1a | 38.7b | 2.49c | |
| | | --------------------------g l$^{-1}$ | ------------------------- | | |
| | 0-3 | 81.9Ab | 117Aa | 3.53Ac | 67.5A |
| TDS[ǂ] | 3-6 | 39.8Bb | 60.0Ba | 2.92Ac | 34.2B |
| | All Depths | 60.8b | 68.9a | 3.22c | |
| | 0-3 | 5.71Aa | 5.34Ab | 5.82Aa | 5.63A |
| pH | 3-6 | 5.20Ba | 4.91Bb | 5.17Ba | 5.09B |
| | All Depths | 5.80a | 5.49b | 5.86a | |

[§]= Electrical conductivity of using saturated paste extract values.

[†]= Different lowercase letters within rows indicate significant differences at the 0.05 level.

[‡]= Different uppercase letters within columns indicate significant differences at the 0.05 level.

[ǂ]= Total dissolved solids

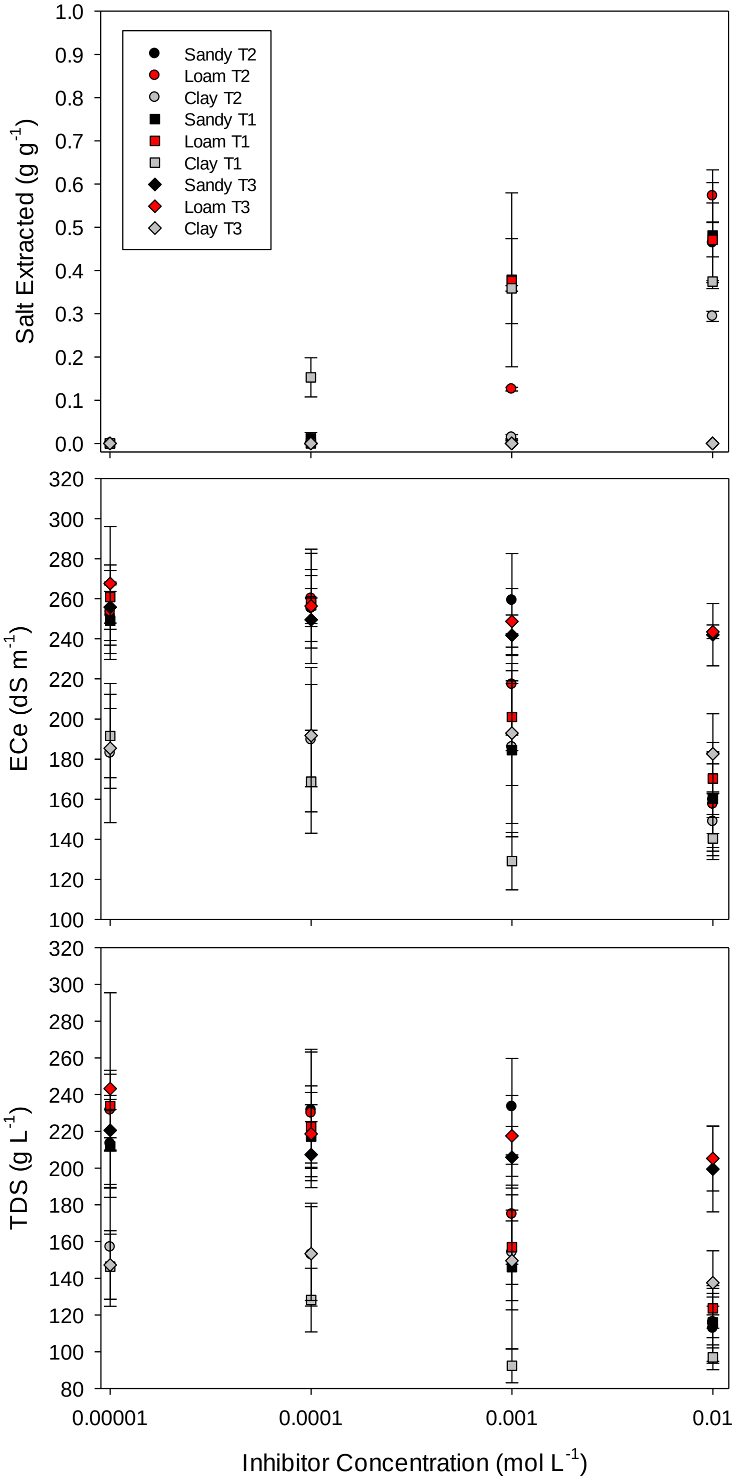

**Figure C1.** Salt extraction (g g$^{-1}$) and measured EC$_e$ and TDS for each crystallization inhibitor concentration using three soil textures and three application methods. Salt growths were harvested seven days after efflorescence began to occur and soil columns were disassembled for chemical analyses.

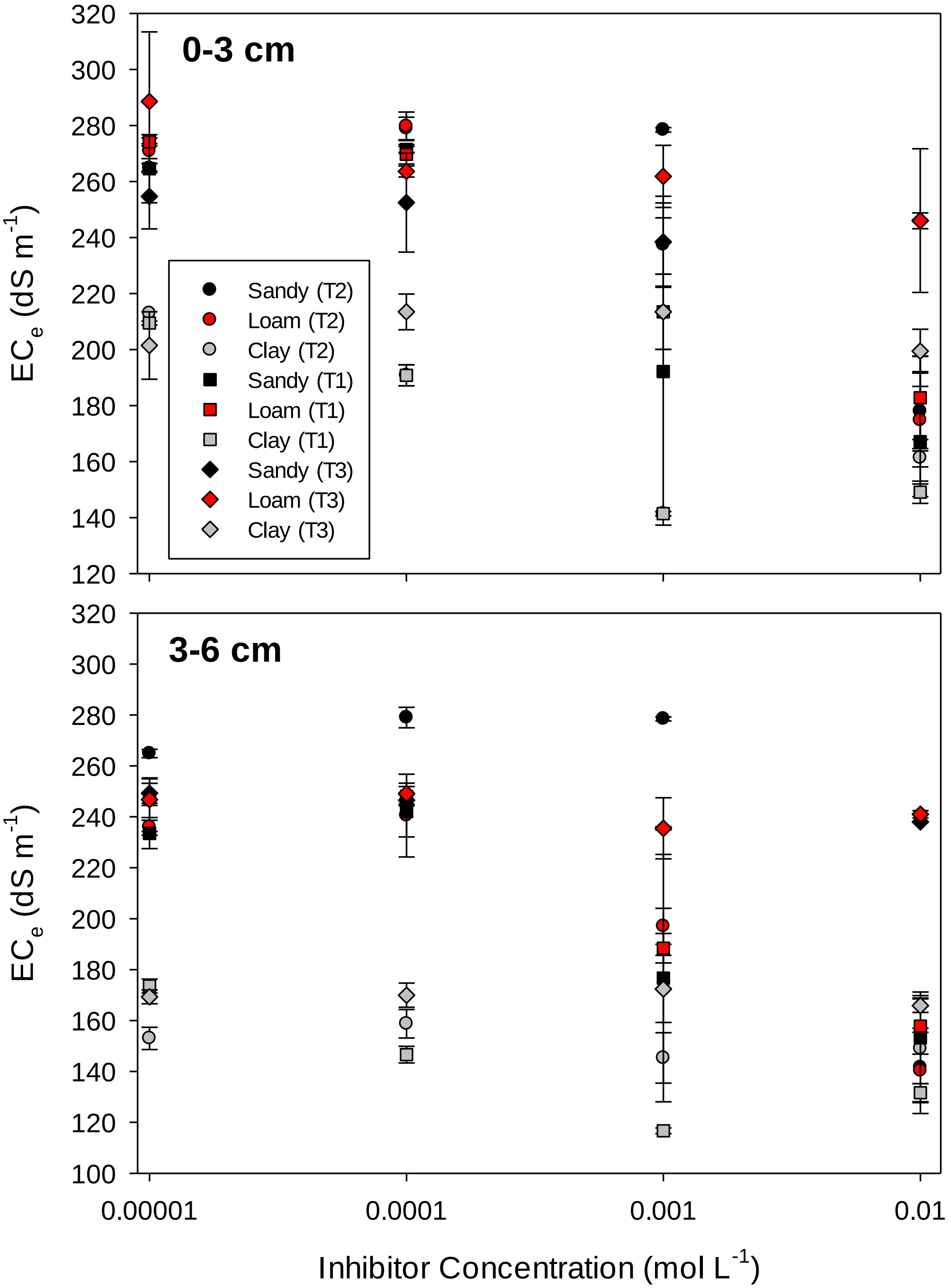

**Figure C2.** Soil $EC_e$ of the columns top soil depth (0-3 cm) and bottom soil depth (3-6 cm) as a function of crystallization inhibitor concentration. Salt crystals were harvested seven days after efflorescence began to occur and soil columns were disassembled for chemical analyses.

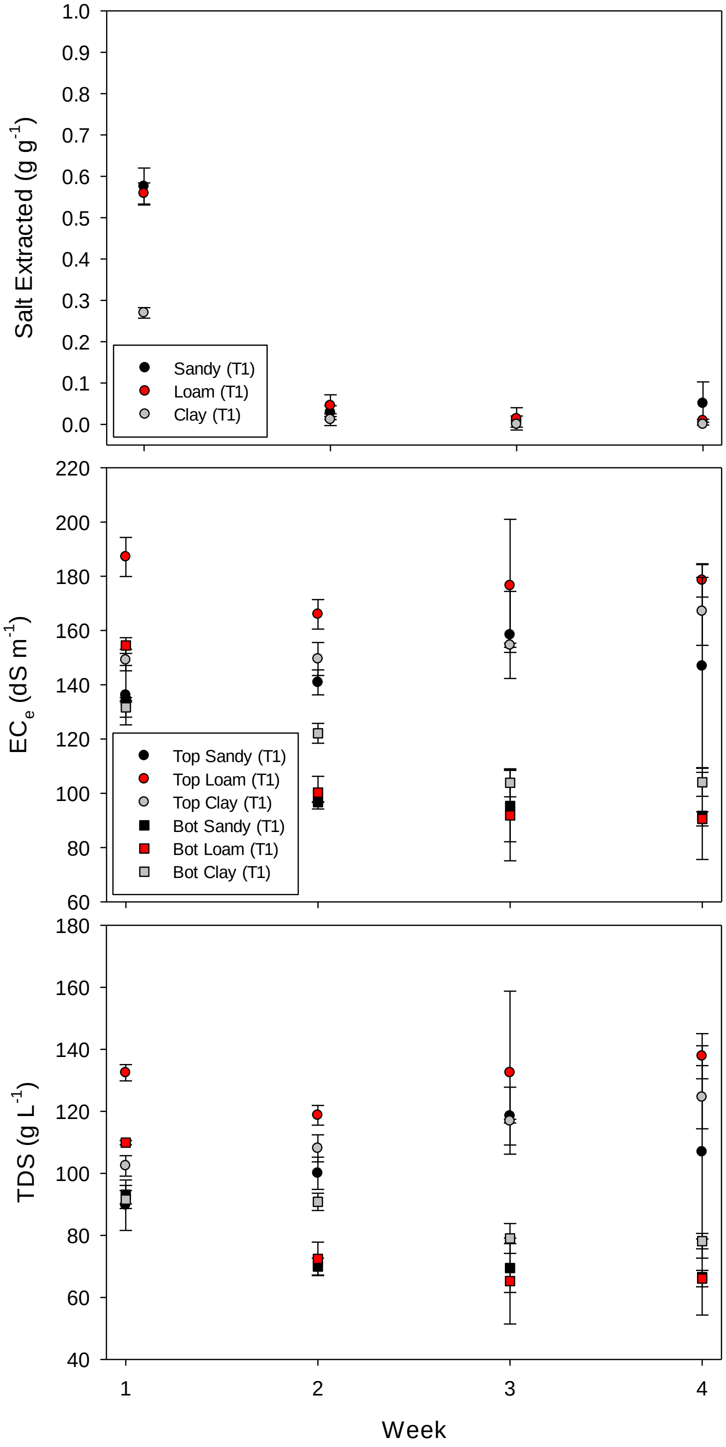

**Figure C3.** Amount of salt harvested (g g$^{-1}$) and soil EC$_e$ and TDS after repeated salt harvest and $H_2O$ re-application. Harvestable salt quantities were minimal following the harvest of salt formations one week after efflorescence.

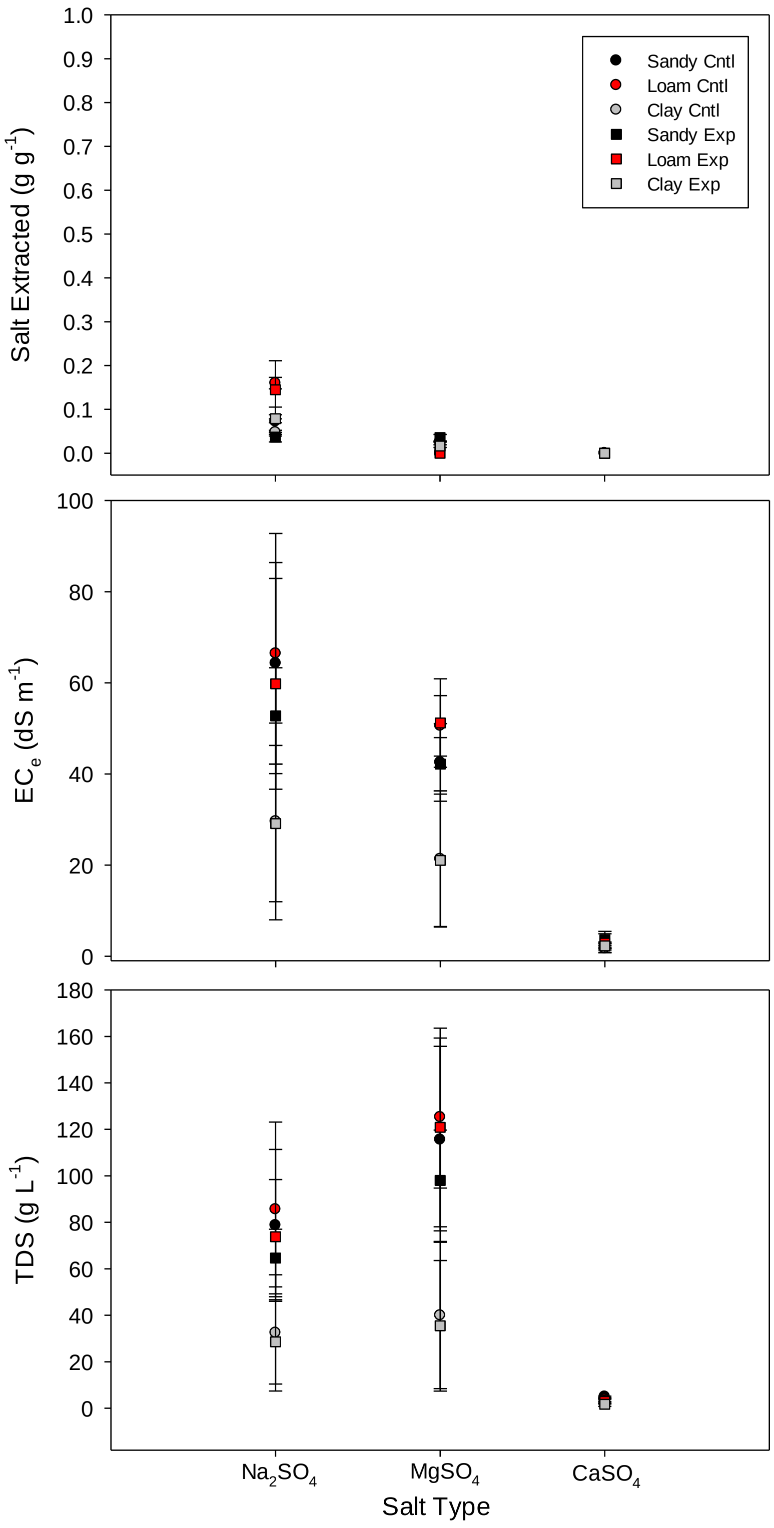

**Figure C4.** Salt extraction rates (g g$^{-1}$) and measured EC$_e$ and TDS for each salt type using three soil textures and the T1 application method. Salt formations were harvested seven days after efflorescence began to occur and soil columns were disassembled for chemical analyses.

# APPENDIX D.CHAPTER II TOTAL DISSOLVED SOLIDS EQUATION DEVELOPMENT

## EC Extract and TDS Relationships

Non-linear regression analysis of $EC_e$ vs. TDS for experiment I and II are shown in Figure's 1 and 2, respectively. The relationship between $EC_e$ and TDS for Experiments I and II had coefficient of determination ($r^2$) values of 0.97 and 0.98, RMSE of 6.54 and -1.69 dS $m^{-1}$ and bias values of 5.01 and -0.52 dS $m^{-1}$, respectively. Based on these analyses, soil $EC_e$ can be accurately estimated from a measured TDS value across a high range (80 to 250 dS $m^{-1}$) using the following equations:

$$\boldsymbol{Experiment\ I\ EC_e = -0.0032(TDS)^2 + 1.9769(TDS) - 29.4955} \qquad \text{(D1)}$$

$$\boldsymbol{Experiment\ II\ EC_e = -0.0047(TDS)^2 + 2.2195(TDS) - 34.0974} \qquad \text{(D2)}$$

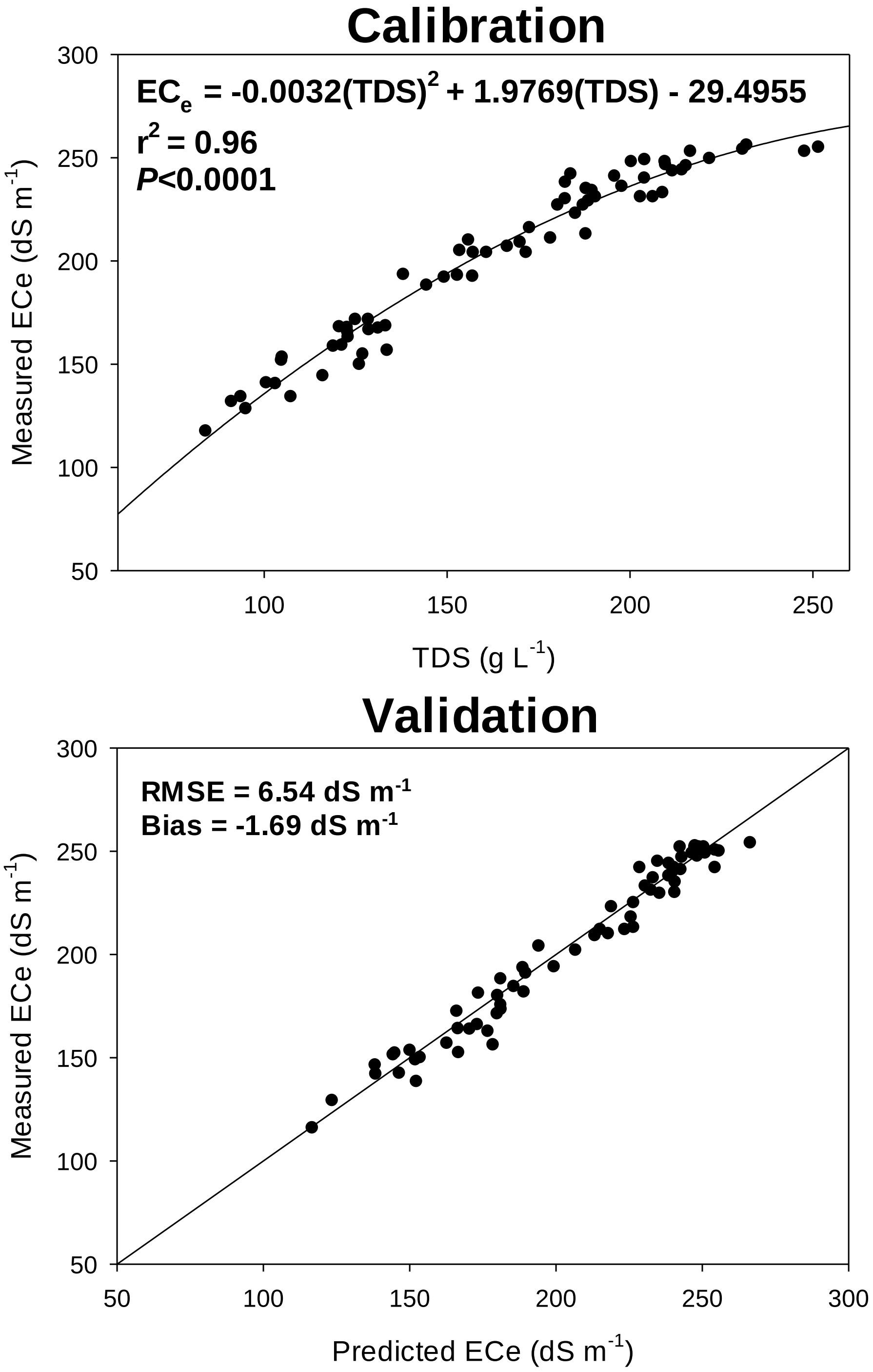

**Figure D1.** Equation development and validation for measured $EC_e$ vs. TDS and measured vs. predicted $EC_e$ for Experiment I. Nonlinear (quadratic) regression was used to develop the correlation between measured $EC_e$ and TDS.

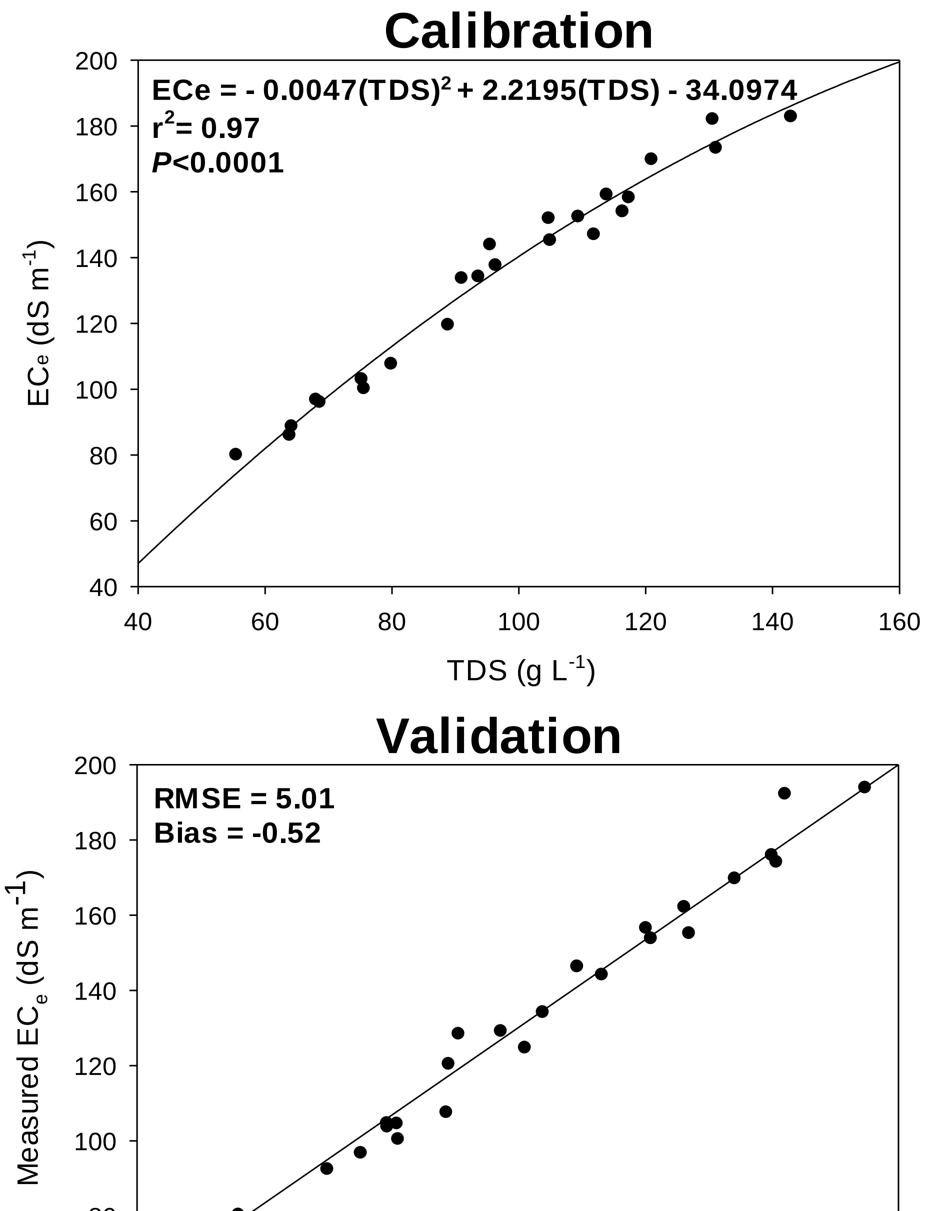

**Figure D2.** Equation development and validation for measured $EC_e$ vs. TDS and measured vs. predicted $EC_e$ for Experiment II. Nonlinear (quadratic) regression was used to develop the correlation between measured $EC_e$ and TDS.