OIL-FIELD BRINE IMPACTS ON SEED GERMINATION AND A CONTEMPORARY REMEDIATION TECHNIQUE FOR CONTAMINATED SOILS

A Thesis
Submitted to the Graduate Faculty
of the
North Dakota State University
of Agriculture and Applied Science

By

Aaron Wesley Green

In Partial Fulfillment of the Requirements
for the Degree of
MASTER OF SCIENCE

Major Program:
Natural Resources Management

July 2019

Fargo, North Dakota

North Dakota State University
Graduate School

Title

OIL-FIELD BRINE IMPACTS ON SEED GERMINATION AND A CONTEMPORARY REMEDIATION TECHNIQUE FOR CONTAMINATED SOILS

By

Aaron Wesley Green

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:

Dr. Miranda Meehan
Co-Chair

Dr. Thomas DeSutter
Co-Chair

Dr. Aaron Daigh

Dr. Jack Norland

Approved:

July 23, 2019	Dr. Edward Dekeyser
Date	Department Chair

ABSTRACT

The growth of fossil fuel production in North Dakota has resulted in numerous releases of brine. Brine releases cause vegetation mortality as well as the deterioration of soil structural and edaphic properties. Little research to date has been dedicated to the germination response of plant species grown in North Dakota to brine-induced salinity. Through the exposure of plant seeds to increasing levels of brine and NaCl-induced salinity, it was determined that the graminoid species *Elymus hoffmannii* (AC Saltlander) and *Pascopyrum smithii* (Western Wheatgrass) exhibited the greatest germination at high salinities. Current remediation technologies for brine-impacted lands often produce mixed results, requiring further research and testing. In two laboratory experiments, the ability of materials to wick salts from brine-contaminated soils was tested. The results of these studies show that some materials reduced Na concentrations in sandy loam, loam, and silty clay soils by upwards of 88, 89.5, 38.4% respectively.

ACKNOWLEDGEMENTS

The contents of this thesis represent the hard work and cooperation of numerous professors, classmates, and faculty at NDSU who have provided to me numerous opportunities for self-growth and friendship over the past six years. In particular, this thesis is a testament to the guidance, wisdom, and enthusiasm of my co-advisors Dr. Miranda Meehan and Dr. Thomas DeSutter. They have provided me with invaluable knowledge and skills, a clear sense of purpose, numerous opportunities for self-growth, friendship and a self-confidence that I will never forget and always appreciate. I am also thankful for the guidance and knowledge provided by the other members of my committee, Dr. Jack Norland and Dr. Aaron Daigh. Collectively, they both have supported my efforts throughout my academic career and have instilled in me the desire to pursue a life of self-learning as well as an invaluable sense of perspective that will guide me with my future pursuits in the scientific field.

I would also like to thank Kevin Horsager, whose help, patience, and friendship were deeply appreciated. Similarly, I would also like to thank the other faculty members, students, professors in the departments of soil science, natural resources management, animal science, and the North Dakota State Seed Lab including, Jeanna Mueller, Nathan Derby, Zachary Leitner, Meyer Bohn, Samantha Croat, Megan Ostrand, Casey Wallace, Dr. Edward Dekeyser, Dr. Peter O'Brien, Ashley Hoyle, Dr. Megan Nelson, Laura Grube, Dr. James Gaspers, Jessica Reiners, Alex V., Michaella Fevold, and Garret Hecker whose friendship and help were invaluable throughout my graduate studies. Finally, I would like to thank my parents Wesley and Joy Green as well as my sister Alison Green, whose love and support throughout my life has brought me to where I am today. Words cannot describe how much I appreciate and value each of you.

DEDICATION

For my grandparents Oscar and Fern Green.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AOSA	Association of Official Seed Analysts
BBL	Barrels
BBBL	Billion Barrels
C	Control
CEC	Cation Exchange Capacity
DI	Distilled Water
DF	Degrees of Freedom
EC	Electrical Conductivity
ESP	Exchangeable Sodium Percentage
FG	Final Germination (%)
GR	Gypsum Requirement
HM	Second Nature® Wood Fiber Plus Hydraulic Mulch (Profile Products®)
HW	CBW9 Humidi-Wick (BestAir Pro®)
MAX	Maximum
MED	Median
MIN	Minimum
MMBL	million barrels
NDAWN	North Dakota Agricultural Weather Network
NDDOH	North Dakota Department of Health
NDDMR	North Dakota Department of Mineral Resources
NDSWC	North Dakota State Water Commission
NDSU	North Dakota State University
ND	North Dakota
NORM	Naturally Occuring Radioactive Materials

PET	Potential Evapotranspiration
PGPR	Plant Growth Promoting Bacteria
PLS	Pure Live Seed (%)
PVC	Polyvinyl Chloride
SAR	Sodium Adsorption Ratio
SD	Standard Deviation
SOV	Source of Variation
SW	1043 Super Wick (Essick Air Products, Inc.)
S	Ground Wheat Straw
TDS	Total Dissolved Solids
USDA	United States Department of Agriculture
USEIA	United States Energy Information Administration
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey

GENERAL INTRODUCTION

Global population growth and industrialization have greatly increased the demand for both food and energy. This increasing demand for both agricultural products and energy has led to unprecedented economic growth and development in the state of North Dakota. Through the use of hydraulic fracturing and horizontal drilling, the production of oil and gas from the Bakken and Three Forks formations has increased exponentially over the past two decades. While proving to be economically beneficial, oil and gas production poses significant risks to agriculturally dominated regions in the form of produced water or “brine” spills. Anthropogenic salinization resulting from brine spills coupled with the approximately 5.8 million acres of land already affected by salinity in the state accentuates the need for effective management and remediation strategies for these soils (Brennan and Ulmer, 2010). Brine, a regulated by-product of the oil and gas extraction process, is a solution consisting of high levels of dissolved salts, primarily NaCl, and other minor components such as drilling fluids and hydrocarbons (Bader, 2016; Clark and Veil, 2009). On average, for every barrel of oil produced in the region, three barrels of brine may also be produced. The use of reinjection wells has been proven to be the most cost-effective and environmentally secure method for brine disposal, however, failures of well pad storage facilities and transportation infrastructure (pipelines etc.) to reinjection wells has resulted in a significant number of accidental brine releases to the present day (Lauer et al., 2018; Patterson et al., 2017).

Brine-contaminated soils often exhibit structural and edaphic properties that severely inhibit the growth of vegetation, creating landscapes susceptible to both wind and water erosion (Qadir et al., 2007; Murphy et al., 1988). Without active remediation, the effect of salts on soil and vegetation can last many years due to the semi-arid climate of the region (Murphy et al., 1988). The establishment of vegetation is a key component in the successful remediation of brine-contaminated soils. To achieve successful revegetation in a cost-effective and efficient manner, information concerning the salt tolerance thresholds of various plant species becomes an important consideration. In the literature, significant focus has been dedicated to the determination of salinity thresholds for a wide variety of plant species in response to differing concentrations of specific salt species (i.e. NaCl, Na_2SO_4, $MgSO_4$, etc.) (Grieve et al., 2012; Keiffer and Unger, 2002). Little research, however, has been dedicated to the germination tolerance thresholds for plant species in the presence of oil-field brine, which often contains a suite of dissolved salt species and chemicals.

Numerous remediation strategies have traditionally been employed for salt-affected soils and are often grouped into on-site (in-situ) and off-site (ex-situ) methods. The choice of remediation method depends on the severity of contamination, environmental factors (i.e. climate, relief, soil texture, etc.), cost-effectiveness, and relative efficiency of salt removal (Vavrek et al., 2014). In-situ remediation practices often rely on use of chemical amendments such gypsum ($CaSO_4$) or organic amendments (manure, straw, etc.) to promote soil flocculation and the downward leaching of NaCl out of the topsoil (Vavrek et al., 2014). Current methods, however, can fail to achieve sustained remediation success in a cost-effective and timely manner, making continued research into alternative methods necessary (Klaustermeier et al., 2017).

The research objectives in this thesis include: 1) the determination of germination thresholds for a number of crop and graminoid species in the presence of brine and NaCl solutions at increasing levels of electrical conductivity (EC) and 2) the determination of the remediation potential in using the surficial application of wicking materials to absorb and remove salts from brine-contaminated soils. To achieve objective 1, the germination of four crop and four graminoid species were tested using guidelines specified by the Association of Official Seed Analysts (AOSA) at various levels of salinity. To achieve objective 2, two separate soil column experiments were conducted in laboratory settings utilizing various soil textures, wicking materials, and irrigation solutions while measuring total sodium removal and evaporation rate.

THESIS ORGANIZATION

This thesis consists of four chapters and is organized in a manuscript format. Chapter 1 is a literature review regarding the production of brine during the oil and gas extraction process, brine genesis and characteristics, causes of brine releases, effects of brine-contamination on vegetative growth and soil properties, considerations for remediation, current remediation techniques, and contemporary remediation methods. Chapter 2 is titled "Germination of Selected Crop and Graminoid Species in Response to NaCl and Oil-field Brine Induced Salinity" and focuses on the germination response of various plant species to increasing levels of NaCl and brine induced salinities. Chapter 3, titled "Wicking Salts from Brine-Contaminated Soils: Potential Method for In-Situ Remediation," spotlights a preliminary soil column study which was used as a proof of concept for the proposed remediation method of wicking salts from brine-impacted soils and has been submitted and published in Agricultural & Environmental Letters. Chapter 4, titled "Brine Spill Remediation Utilizing Capillary Transport and Wicking Materials: Efficacy in Loam and Silty Clay Soils", presents the results from a second soil column experiment focusing on the effectiveness of the proposed remediation technique in loam and silty clay soils and provides additional evidence for the continuation of research into the effectiveness of this method in field-scale trials.

CHAPTER 1: TRADITIONAL AND CONTEMPORARY REMEDIATION OF BRINE-IMPACTED SOILS: A REVIEW

Introduction

Since 2012, North Dakota has been the second leading producer of crude oil in the United States (US EIA, 2018). The production of crude oil in the state occurs primarily from the Bakken and Three Forks formations located in the Williston Basin, which collectively, have been characterized as one of the most significant reserves of oil and gas in the world (Durham, 2010; Gleason et al., 2014). The primary byproduct of oil and gas production is known as produced water or “brine” (Gleason et al., 2014; Guerra et al., 2011; Clark and Veil, 2009). Brine is a saturated solution of dissolved salts, oil, and drilling chemicals that exhibits elevated levels of total dissolved solids (TDS), electrical conductivity (EC), and sodium adsorption ratio (SAR) (Lauer et al., 2016; Gleason et al., 2014; Guerra et al., 2011; Clark and Veil, 2009).

The accidental release of brine into the environment can have severe deleterious effects on soil quality and vegetative health. To remediate these impacts, a variety of in-situ and ex-situ techniques are used to remove or reduce salt concentrations in the topsoil and restore previous levels of vegetation production (Derby et al., 2016; Vavrek, 2004). The remediation of brine-contaminated soils is often costly in terms of time and financial resources, making the choice of remediation strategy an important decision for the various stakeholders in the region. The objectives of this literature review are to provide a detailed analysis of 1) brine production and releases in the Williston Basin, 2) the effects of brine releases on soil quality and vegetation, 3) current ex-situ and in-situ methods used for remediation, and 4) contemporary and experimental methods for remediation.

Oil and Gas Production in North Dakota

Regional Characterization

The Williston Basin is the primary oil and gas producing region of the upper Great Plains, covering parts of Manitoba, Saskatchewan, Montana, North Dakota, and South Dakota (Gleason et al., 2014; Gaswirth et al., 2013; Lefever, 1991). By area, the basin covers nearly two thirds of North Dakota and encompasses numerous oil-bearing geologic formations, with the highest producing consisting of the Bakken and Three Forks formations (Lefever, 1991). The Bakken and Three Forks are comprised primarily of shale and siltstones exhibiting low porosities (≤5%) and permeabilities, with the highest oil production occurring from the geographic center of the Williston Basin near Williston, North Dakota (Pitmann et al., 2001). The climate of this region is characterized as continental and semi-arid, with average annual precipitation and potential evapotranspiration (PET) of ≤36 cm yr^{-1} and ≥140 cm yr^{-1}, respectively (NDAWN, 2018; NDGF, 2016). Northeast of the Missouri River, soil parent materials consist of recently deposited glacial till and to the southwest consist primarily of highly weathered residuum (Gleason et al., 2014; Bluemle, 2016). Many soils in North Dakota contain significant amounts of clays including smectite, illite, and kaolinite, (Franzen and Bu, 2018) making them highly valuable for crop production and livestock grazing. Within the extent of the Williston Basin of North Dakota and Montana, land use is largely agricultural, with this region producing a significant portion of the nation’s wheat (*Triticum aestivum*), dry beans (*Phaseolus vulgaris*), and peas (*Pisum sativum*) (USDA, 2017; Preston and Kim, 2016).

Current and Historical Trends in Oil and Gas Development

The presence of oil and gas reserves in North Dakota dates back over a century. As early as the 1890’s, gas from artesian wells were used as an energy source to provide heat to a number of small towns and farms across western North Dakota (Bluemle, 2016; Anderson and Eastwood, 1963). Commercial production of natural gas in the state began in the 1920's, however, limited interest inhibited further exploration for another 30 years (Gleason et al., 2014; Lefever, 1991; Anderson and Eastwood, 1963). The first successful oil producing well in North Dakota was completed in 1951 and was followed by the successful establishment of numerous other exploratory wells throughout the Williston Basin (Lefever, 1991; Gerhard et al., 1990). The geological characteristics of the Bakken and Three Forks formations resulted in initial production and development to increase gradually, as conventional (i.e. vertical) drilling methods were incapable of extracting economical amounts of oil and natural gas for sustained development (Lefever, 1991). In the 1980's, production substantially increased as the use of unconventional drilling technologies, horizontal drilling and hydraulic fracturing, became more widely adapted throughout the Williston Basin (NDSWC, 2016; Gleason et al., 2014; Lefever, 1991). The practice of drilling horizontally into oil-bearing formations allows for a significant increase in total area in which individual wells can drain while hydraulic fracturing improves oil recovery by increasing the porosity and permeability of shale and sandstone formations (Vengosh et al., 2014; Guerra et al., 2011; Deans et al., 1991; Lefever, 1991). Using these techniques, oil and natural gas production began increasing exponentially by the year 2007 (Lauer et al., 2016) and between 1980 and 2006, the average annual oil production in the state was approximately 37.5 million barrels (MMBL) (NDDMR, 2017). Following 2007, annual production increased to nearly 250 MMBL of oil per year with a maximum production of 432 MMBL in 2015.

The estimated amount of recoverable oil reserves available in the Bakken and Three Forks formations is of considerable debate, however, estimates of the total oil resources contained in the formations have exceeded 400 billion barrels (BBBL) (Price, 1999). In 2013, the United States Geological Survey estimated the Bakken and Three forks formations contained recoverable oil reserves of approximately 7.375 BBBL, while other estimates range anywhere from 3 to 24 BBBL (McNally and Brandt, 2015; Gaswirth et al., 2013). Although a considerable amount of uncertainty exists in recoverable oil reserve estimates and future oil prices, development in the Williston Basin is expected to continue to expand for many years into the future.

Unconventional Drilling Techniques

The growth of the oil and natural gas industry across the Williston Basin can be attributed to the use of the unconventional drilling techniques of horizontal drilling and hydraulic fracturing (Patterson et al., 2017; Rodriguez and Soeder, 2015; Vengosh et al., 2014; Gaswirth et al., 2013; Deans et al., 1991). Horizontal drilling is the process of drilling vertically to a considerable depth and then parallel or nearly parallel across oil-bearing geologic formations (Rodriguez and Soeder, 2015). These wells can be drilled laterally to a distance greater than 3 km from well sites, improving the probability of intersecting rock fractures and thereby increasing the productivity and profitability of individual wells (Gregory et al., 2011; Deans et al., 1991). Hydraulic fracturing utilizes the injection of large volumes of fluids, proppants (sand, ceramics, etc.), and chemicals (e.g. surfactants, biocides, acids) at high pressure to create and maintain fractures in tight rock formations, significantly increasing the overall porosity and permeability of the rock and releasing much greater volumes of oil than horizontal drilling alone (Vengosh et al., 2014; Gregory et al., 2011; Deans et al., 1991). Hydraulic fracturing is often carried out in stages to maximize production and increase the life of individual wells (Rodriguez and Soeder, 2015; Gregory et al., 2011). The effectiveness of unconventional drilling techniques has greatly increased the amount of technically recoverable oil and natural gas reserves throughout the world and is expected to be a significant driver of energy development throughout the Williston Basin for the next few decades (McNally and Brandt, 2015).

Principle Waste of Oil and Natural Gas Production: Brine

Genesis and Chemistry

The utilization of conventional and unconventional drilling techniques for oil and natural gas production in the Bakken is associated with a number of byproducts and potentially hazardous wastes. The most significant component of the oil and natural gas waste stream consists of produced water or "brine" (Gleason et al., 2014; Guerra et al., 2011; Clark and Veil, 2009). Oil-field brine is derived from water released by geologic formations (i.e. formation water) and the dissolution of mineral and organic compounds into fluids used in the hydraulic fracturing process (Gregory et al., 2011; Guerra et al., 2011; Veil et al., 2004). Fresh water is the most common fluid used for hydraulic fracturing, a majority of which is delivered to the well from local surface or ground water sources (NDSWC, 2016; Gleason et al., 2014; Gregory et al., 2011). The volume of fresh water required for each stage of fracturing can be highly variable from well to well, however, the North Dakota State Water Commission (2016) estimates that over the entire drilling process, fracturing in the Bakken uses approximately 113,789 BBL or 13552 m^3 for each well. Preceding the drilling and fracturing stages, fluids in the well bore are depressurized and flow back to the earth's surface with the oil, where it is then separated and treated through gravitational methods, physical methods (e.g. filtration, centrifugation, etc.), thermal distillation, and/or chemical methods before disposal (Kurz, 2016; Gregory et al., 2011; Clark and Veil, 2009; Veil et al., 2004). The volume of brine produced from wells often varies with geographic area, geologic formation, and the age of a particular well, with older wells producing more brine as the amount of recoverable oil decreases (Kondash et al., 2017). In the

Williston Basin, significant volumes of brine are produced per barrel of oil, with most wells exhibiting brine to oil ratios between 3:1 and 18:1 (Guerra et al., 2011; Clark and Veil, 2009; Otton, 2006; Veil et al., 2004). Based on an assumed well life of 30 years, Kondash et al. (2017) estimated an average brine production for individual wells in the Bakken of approximately 143,848 BBL.

The chemistry of oil-field brine makes it extremely hazardous to the soil and water resources of the region due to elevated concentrations of dissolved salts and organic compounds. Brines produced in the Williston Basin have been characterized as some of the most concentrated in the United States, exhibiting TDS averaging 250 g L^{-1} and EC exceeding 200 dS m^{-1} (Klaustermeier et al., 2017; Lauer et al., 2016; Gleason et al., 2014; Guerra et al., 2011). From data provided in the U.S. Geological Survey National Produced Waters Geochemical Database (v2.3), brines in the Williston Basin exhibit mean levels of TDS of 230 g L^{-1} (Table 1) (Blondes et al., 2017). The most concentrated brines from this dataset were found within the extent of the Bakken formation (Figure 1). Dominant ionic composition varies throughout the Bakken and Three Forks regions, with Na-Cl brines found in the Canadian portions of the basin and Na-Ca-Cl dominated brines found near its geographical center in Williston, North Dakota (Iampen and Rostron, 2000). In North Dakota, however, brine composition is predominantly composed of NaCl (~90%) and lesser amounts of dissolved Ca, Mg, and K (Bader, 2016; Guerra et al., 2011; Clark and Veil, 2009). From the sources provided in Table 1, the average concentrations of Cl, Na, K, Ca, and Mg are 137.2, 72.0, 3.49, 11.7, and 1.21 g L^{-1}, respectively. Reflecting the prevalence of Na, average SAR values for brine produced in North Dakota are among the highest in the nation, with values often approaching or even exceeding 300 (Guerra et al., 2011). In Table 1, mean SAR values ranged from 263 to 176. In addition to elevated concentrations of salts and hydrocarbons, analyses of numerous brine samples have shown that brine produced in the region also contains high amounts of naturally occurring radioactive materials (NORM) and trace metals including boron, arsenic, radium, and strontium (Lauer et al., 2016). These trace elements have received significant attention in the literature due to the significant risks they pose to human health (Cozzarelli et al., 2017; Lauer et al., 2016; Guerra et al., 2011).

Management Practices and Contamination

Given the large volume and high concentrations of potential contaminants found in oil-field brine, its management has proven to be a significant issue confronting industry, government agencies, and landowners. In the early to mid-20th century, much of the brine produced across the United States from oil extraction was disposed of through direct discharge into surface waters (streams etc.) or were stored in large evaporation pits (Gleason et al., 2014; Whittenmore, 2007; Kharaka et al., 2005; Murphy et al., 1988; Pettyjohn, 1971). Evaporation pits were used to reduce the volume of brine through evaporation, however, a significant amount of brine often infiltrated into the surrounding soil and ground water systems, causing severe salt contamination (Murphy et al., 1988; Pettyjohn, 1971; Reiten and Tischmak, 1993). Following the cessation of production, many of these pits were filled in and abandoned, eventually resulting in the formation of salt plumes which extend for considerable distance both laterally and vertically beneath the pits (Murphy et al., 1988). In semi-arid regions such as the Williston Basin, where annual precipitation (≤36 cm) is much less than that of PET (≥140 cm), sufficient leaching and dilution of salts does not often occur naturally, and in many cases, the salts from these pits continue to persist in the soil and ground water systems to the present day.

Table 1: Number, mean, median, and standard deviation of total dissolved solids, chloride, sodium, potassium, calcium, magnesium, and sodium adsorption ratio of brine samples obtained across the Williston Basin from various sources.

Source	Total Dissolved Solids				Chloride				Sodium				Potassium				Calcium				Magnesium				Sodium Adsorption Ratio			
	n	Mean	MD	SD	n	Mean	MD	SD	N	Mean	MD	SD	n	Mean	MED	SD	n	Mean	MD	SD	n	Mean	MED	SD	n	Mean	MD	SD
	#	-------- g L⁻¹ --------			#	-------- g L⁻¹ --------			#	------- g L⁻¹ -------			#	------- g L⁻¹ -------			#	------- g L⁻¹ -------			#	------ g L⁻¹ ------			#	------- g L⁻¹ ------		
NDSU, 2019†	26	271	295	74.0	26	159	173	37.9	26	83.7	84.8	16.7	26	6.81	7.89	3.04	26	12.6	14.3	4.77	26	1.20	1.20	0.26	26	200	189	53.0
Peterman and Thamke, 2016	33	106	61.5	85.2	33	64.1	36.0	53.1	33	38.3	22.6	31.2	33	0.59	0.47	0.50	33	1.57	0.86	1.80	33	0.18	0.12	0.17	33	248	205	148
ND DMR, 2013	7103	245	289	102	7103	149	176	63.4	7103	75.5	86.3	32.9	3958	3.27	2.86	2.97	7103	15.6	12.2	15.1	7103	1.41	1.14	1.48	7103	184	178	121
Shouakar-Stash, 2008	33	268	301	79.4	33	162	185	48.0	33	75.3	80.8	23.6	33	4.92	5.31	2.66	33	20.1	18.2	16.0	33	1.95	1.53	1.31	33	176	159	97.8
Jensen, 2007	11	284	274	27.2	11	183	182	12.6	11	96.4	92.8	9.90	11	4.94	4.88	0.35	11	14.4	13.8	3.79	11	1.46	1.49	0.21	11	209	214	36.6
Iampen, 2003	44	302	305	62.3	44	177	180	20.4	44	81.9	85.5	16.3	44	5.77	5.88	2.49	44	22.9	19.0	15.3	44	2.08	1.76	1.10	44	181	154	112
Briet and Otton, 2002	3400	166	150	132	3399	98.9	88.0	80.5	3400	55.2	50.3	44.0	750	2.10	1.16	2.42	3400	6.59	3.03	9.31	3400	1.03	0.57	1.33	3400	192	167	143
Rostron et al., 2002	26	213	251	118	26	121	148	67.1	26	68.4	86.1	36.5	26	3.05	3.27	1.89	26	6.62	3.01	9.01	26	0.76	0.46	0.79	26	263	269	141
Reiten and Tischmack, 1993	20	204	210	73.1	20	121	126	48.9	20	73.4	77.6	25.7	0	0	0	0	20	5.07	4.34	2.89	20	0.78	0.66	0.55	20	259	248	59.4

†Unpublished data obtained from brine samples collected by various researchers at North Dakota State University and provided by the ND Department of Health.

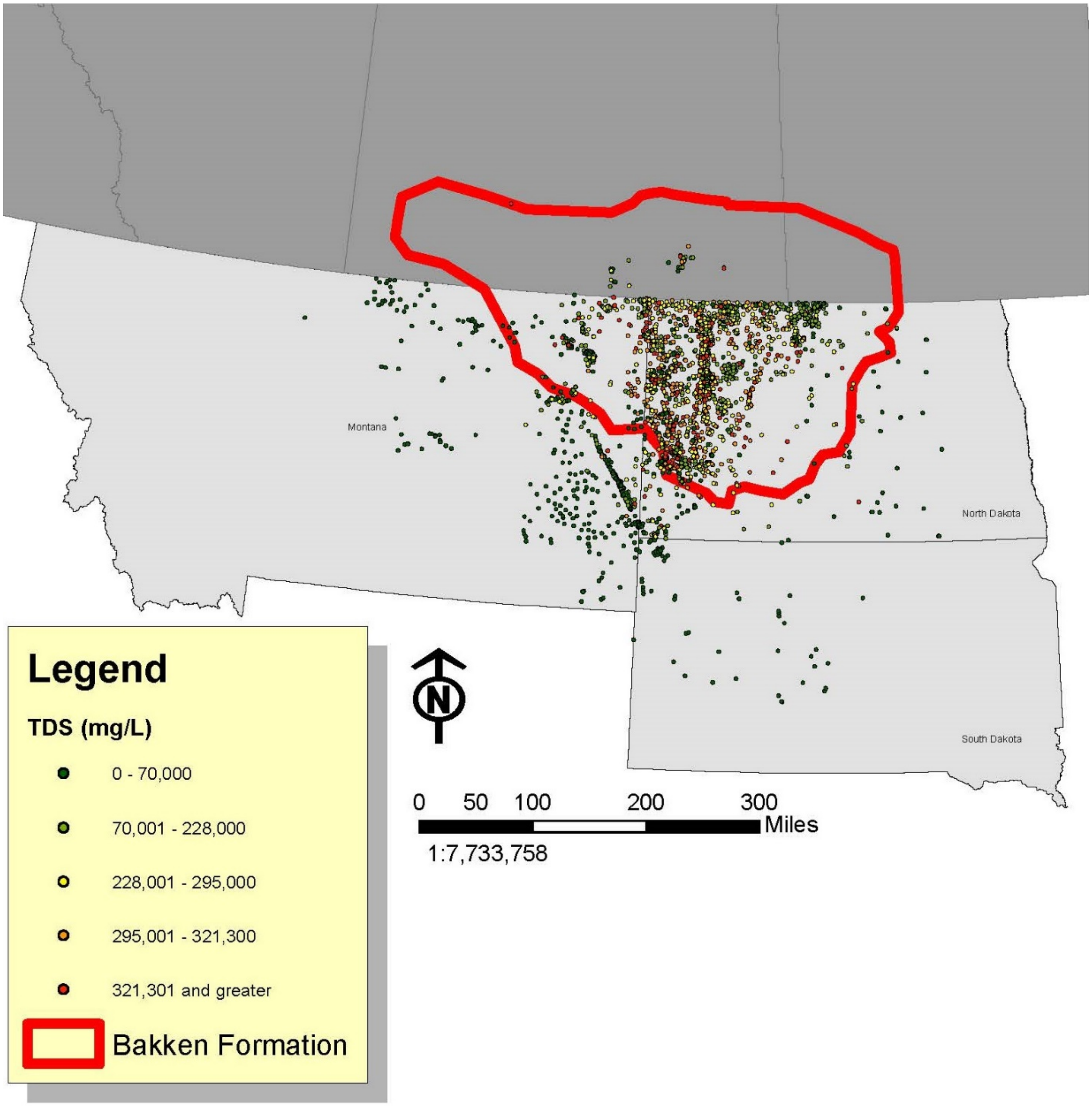

Figure 1: Location and total dissolved solids (TDS) of brine samples collected across the Williston Basin (Blondes et al., 2017).

Environmental contamination caused by these early methods culminated in the passage of state and federal regulations prohibiting their use throughout many of the country's oil producing regions (Pettyjohn, 1971). The disposal of brine has been regulated in the state of North Dakota since the 1970's, however, the frequency and volume of brine spills in the region has increased exponentially with oil production over the past decade (ND DOH, 2018; Klaustermeier, 2016). Currently, a vast majority (~98%) of onshore derived brine in the United States is disposed of using class II reinjection wells, which are regulated through the Underground Injection Program, a provision of the Safe Drinking Water Act of 1974 (Bader, 2016; Clark and Veil, 2009; US EPA, 2018; Veil et al., 2004). In most situations, reinjection wells are of considerable distance from oil and natural gas producing wells, necessitating the storage and transportation of brine prior to disposal. The most prevalent storage methods used at well sites in North Dakota include the use of large storage tanks (Kurz, 2016). Transportation of brine from production sites to reinjection wells occurs primarily using tanker trucks or pipelines (Rodriguez and Soeder, 2015).

The primary causes of brine releases include storage tank leaks, pipeline leaks, trucking accidents, and well casing failures (Patterson et al., 2017; Lauer et al., 2016; Rodriguez and Soeder, 2015; Gleason et al., 2014; Guerra et al., 2011; Kharaka et al., 2005; Reiten and Tischmak, 1993). A majority of these spills occur during the first few years of oil production and nearly half are constituted by multiple incidents occurring from the same wells or pipelines (Patterson et al., 2017). Since 2001, the North Dakota Department of Health has recorded the frequency and volume of uncontained (off drilling pad) brine and hydrocarbon spills throughout the state. In the period between 2001 and 2015, a total of 6,247 brine spills occurred with an average volume each of 12,590 L (ND DOH, 2018; Klaustermeier, 2016). According to Lauer et al. (2016), approximately 3,900 of these spills occurred following the expansion of oil development in 2007. The largest of these incidents occurred from a pipeline leak near Black Tail Creek in northwestern North Dakota, which released nearly 11,400 m^3 of brine into the surrounding environment (Cozzarelli et al., 2017).

Effects of Brine Contamination on Soil and Plant Health

Soil Chemistry and Structure

The discharge of brine into the environment results in significant alterations to soil chemistry and structure. These changes are caused by the chemical consistency (i.e. ionic species) and high concentrations of solutes found in brine that interact with the soil matrix. Following a spill, the dissolved ions in brine saturate the soil solution and through mass action, Na cations (Na^+) adsorb to soil exchange sites.

The clay fraction is the most chemically reactive portion of soil matrix and causes soils to exhibit significant changes in both chemical and structural properties following a brine spill (Qadir et al., 2007; Goldberg et al., 2000). The behavior of the clay fraction in soils is dependent on mineralogical consistency, the ionic concentration and speciation of the soil solution, and the adsorbed cationic species on cation exchange sites (Shainberg and Letey, 1984). The surface of clay particles are often negatively charged due to a number of processes and characteristics including isomorphic substitution (permanent charge), surface dissolution of ionic compounds (hydroxyl groups), and the presence of negatively charged organic compounds (Sposito, 2008; Schaetzl and Anderson, 2005; Goldberg et al., 2000; Sparks, 1998). This negative charge results in the attraction and adsorption of oppositely charged cationic species found in the soil solution (Smith et al., 2015; Marchuk and Rengasamy, 2011; Qadir et al., 2007; Shainberg and Letey, 1984). In the Bakken and Three Forks region, brine-impacted soils are most commonly dominated by the monovalent cation Na (≥ 90%) and to a lesser degree, the divalent cations Ca and Mg and thus, following a spill, Na dominates the exchange sites.

Soil structure is often characterized as being in a state of flocculation or dispersion. In flocculated soils, clay particles are organized in structural aggregates or tactoids (Shainberg and

Letey, 1984; Oster et al., 1980). In dispersed soils, there are no structural associations between clay particles due to electromagnetic repulsion (Schaetzl and Anderson, 2005). The relationship between adsorbed cations and the structural properties of the soil is often described using the ionicity index, which is used to determine the relative binding strength of particular cations in solution to clay particle exchange sites (Smith et al., 2015; Marchuk and Rengasamy, 2011; Sposito et al., 2008). The ionicity index value (binding strength) of cations in solution follows the relationship: Li > Na > K > Mg > Ca > Sr > Ba where the larger ionicity values (Li) indicate weaker binding strength to exchange sites while smaller values (Ba) represent stronger binding strength (Smith et al., 2015; Marchuk and Rengasamy, 2011; Sposito et al., 2008). Na, the dominant cation in brine-contaminated soils, has one the greatest ionicity indices (i.e. weakest binding strengths) and is present in such high concentrations that it overwhelms most clay particle exchange sites, increasing the potential for swelling and dispersion of clay particles in the soil (Marchuk and Rengasamy, 2011; Hanor, 2007). Swelling and dispersion cause a significant decrease in overall porosity and connectivity of soil pores, which in turn reduces the hydraulic conductivity and infiltration capacity of the soil (Derby et al., 2016; Hanor, 2007; Shainberg and Letey, 1984; Quirk and Schofield, 1955). Although Na is the dominant cation in brine-impacted soils, clay particles often remain in a flocculated state due to ionic saturation and elevated EC levels (Derby et al., 2016; Merrill et al., 1990). Over a number of leaching events from precipitation, however, the EC of the soil solution may be sufficiently reduced that sodic soil, imparted by the Na within the brine, conditions may prevail, resulting in swelling and dispersion (He et al., 2015; Merrill et al., 1990). For soils with different clay contents, clay mineralogies, and organic matter contents, the point at which swelling and/or dispersion results in a significant decrease in soil hydraulic conductivity has been described through the determination of “threshold” concentration or flocculation value of salts in the soil solution (Shainberg and Letey, 1984; Quirk and Schofield, 1955). If the salt concentration in the soil solution (i.e. EC) drops below the threshold concentration or flocculation value for a soil, clay particles will begin to swell and/or disperse, even at relatively low SAR values (He et al., 2015; Shainberg and Letey, 1984). Alternatively, swelling of clay particles may occur above the flocculation value of a soil over a range of SAR values, however, this process decreases at higher levels of overall salinity (Shainberg and Letey, 1984). Recent research suggests that reductions in EC <2 dS m^{-1} can result in the dispersion of montmorillonite clays at SAR values as low as 5 (He et al., 2013). Furthermore, He et al. (2015) indicate that to prevent swelling of Na-affected soils, the EC of the soil solution should be maintained at/or above 4 dS m^{-1} when the SAR is ≥5. Saurez et al. (2008) observed that the application of irrigation water exhibiting SAR values of 4 and EC values <2 dS m^{-1} resulted in an overall decline in saturated hydraulic conductivity in loam soils as a result of clay swelling.

In semi-arid regions, such as the Williston Basin, capillary action promotes the upward movement of water and dissolved solutes towards the soil surface (NDAWN, 2018; NDGF, 2016; Jambhekar et al., 2015; Thimm, 1990). Over time, continual salt accumulation and precipitation results in the formation of crusts (Qadir et al., 2007; Keiffer and Ungar, 2002; Mullins et al., 1990). Crusting of the soil surface results in a reduction of infiltration rates as well as gas diffusion into and out of the soil, all of which cause a marked decrease in plant growth and increase in soil erosion potential (Leskiw et al., 2012; Young et al., 2011; Aschenbach and Kindscher, 2006).

Seed Germination and Plant Growth

Prior to the expansion of oil and natural gas development in the Williston Basin, the economy of the region was, and largely remains, based primarily on the agricultural production of both livestock and crops (USDA, 2017; Preston and Kim, 2016). The increasing frequency and severity of brine spills in recent years has raised concerns from agricultural producers over the loss of plant productivity and soil function at many sites where these spills have occurred. Brine spills often leave the land devoid of vegetation for extended periods of time through both direct, and indirect effects of induced salinity and sodicity (Young et al., 2011; Aschenbach and Kindscher, 2006; Keiffer and Ungar, 2002). The effects of salinity and sodicity to plant growth can vary significantly between various plant species and growth stages, however, a significant amount of research has been dedicated to characterize numerous plant species as either salt-sensitive (i.e. glycophytic) and salt-tolerant (i.e. Halophytic) (Grieve et al., 2012; Manousaki and Kalogerakis, 2011; Lauchli and Epstein, 1990; Reis and Hoffman, 1983).

Across the various growth stages of a plants' life cycle, seed germination is one of the most crucial, particularly in salt-affected soils (Shaygan et al., 2017; Schmer et al., 2012; Keiffer and Ungar, 2002; Ungar, 1978). In brine-contaminated soils, a number of processes play a role in impeding seed germination and plant establishment. Indirect effects, such as physical changes to soil structure including: salt crust formation, dispersion, and hardsetting, can significantly reduce seed germination rates and the chances of plant establishment (Leskiw et al., 2012; Qadir et al., 2007; Aschenbach and Kindscher, 2006). The formation of salt crusts, dispersion of clay particles, and hardsetting of the soil surface act as structural mechanisms that inhibit the growth and elongation of the radical, epicotyl, and hypocotyl of newly germinated seeds (Aschenbach and Kindscher, 2006; Qadir et al., 2003; Mullins et al., 1990; Shainberg, 1990). In addition, these structural changes reduce the ability of water and gases to infiltrate into the soil, resulting in either a lack of soil water for seed imbibition or the prolonged inundation of the soil surface, both of which severely restrict plant establishment and survival (Grieve et al., 2012; Qadir et al., 2007; Shainberg and Letey, 1984).

The direct effects of brine-contamination on seed germination and plant growth are caused primarily by the ionic saturation of the soil solution, which inhibits plant productivity through a number of deleterious processes (Grieve et al., 2012). The ability of a seed or plant root to uptake water is based on the establishment and maintenance of an osmotic gradient with the soil solution (Lauchli and Epstein, 1990). In soils exhibiting high salt concentrations, the osmotic potential of the soil solution becomes increasingly negative, resulting in the reversal of this osmotic relationship (Aschenbach and Kindscher, 2006; Lauchli and Epstein, 1990). This change in hydraulic gradient severely limits the imbibition of soil water by both plant roots and seeds, often resulting in induced seed dormancy (i.e. delayed seed germination) and the expression of drought-like symptoms in plants at later growth stages (Keiffer and Ungar, 2002; Lauchli and Epstein, 1990; Ungar, 1978).

In conjunction with these effects, high concentrations of NaCl also disrupts the absorption of essential plant nutrients needed for germination and growth (Grieve et al., 2012; Grattan and Grieve, 1998). Grattan and Grieve (1998) indicate that the adsorption of NO_3, K, PO_4, and Ca by plants can be inhibited by the presence of high concentrations of both Na and Cl in the soil solution. In addition, nutrient imbalances and osmotic stress have been shown to significantly inhibit plant metabolic and photosynthetic processes through the closure of stomata, the reduction of CO_2 diffusion into the plant, and the production of hormones which limit cellular growth and division (Chaves et al., 2009; Munns and Tester, 2008).

The ionic saturation of the soil solution caused by brine spills often cause physiological harm to seed and emerging plants through the direct uptake of salts. To promote water uptake and alleviate osmotic stress, some plants will absorb and store various amounts of soluble salts in their tissues (Grieve et al., 2012; Manousaki and Kalogerakis, 2011; Lauchli and Epstein, 1990). This accumulation of salts can have either beneficial or deleterious effects on plant growth depending on the concentrations of the various ionic species found in the soil solution (Grieve et al., 2012). Although brines produced in the Williston Basin contain a number of elements that are essential plant nutrients (i.e. Ca, Mg, K), their elevated concentrations in conjunction with Na and Cl render them toxic (Keiffer and Ungar, 2002; Munn and Stewart, 1989). In addition, various trace elements found in solution such as B and Se, can cause direct toxicity if adsorbed into plant tissue (Grieve et al., 2012; Lauchli and Epstein, 1990; Ungar, 1978). Similar to plants at later growth stages, the effects of ionic adsorption on seed germination vary considerably across plant species and the concentration of salts found in solution (Neumann, 1997; Ungar, 1978). Ion toxicity in seeds, which is caused primarily by the absorption Na and Cl, occurs through the disruption of the metabolic processes required for cell division and germination (Neumann, 1997). In addition, the uptake of salts into seeds may result in the expression of oxidative stress in cells, which is caused by an imbalance in the production of various reactive oxygen species (Ibrahim, 2016). High levels of reactive oxygen species in cells often causes cell death by damaging cellular structures such as membrane lipids and enzymes (Ibrahim, 2016; Ashraf and Foolad, 2005).

Salt Tolerance Mechanisms

Anthropogenic salinity caused from oil and natural gas production has created a significant need for the identification of salt tolerant plant species that can restore the economic and ecological benefits lost to various stakeholders across the Williston Basin. In the literature, the salt tolerance of plant species is based on the level of salinity at which plant germination, growth, and reproduction is able to meet the purposes of their intended use (Grieve et al., 2012). In general, plants are designated as either glycophytes (i.e. salt-sensitive) or halophytes (i.e. salt-tolerant) based on their ability to survive across a range of growth stages at increasing levels of salinity (Manouski and Kaleogerakis, 2012; Munns and Tester, 2008). Glycophytes, or plant species sensitive to salinity, encompass a wide range of crop and graminoid species commonly grown throughout the Williston Basin including alfalfa (*Medicago sativa*) and wheat (*Triticum aestivum*) (Steppuhn et al., 2009; Lauchli and Epstein, 1990). Halophytes, or salt tolerant plant species, employ a number of defense mechanisms that facilitate germination and growth in soils exhibiting high levels of salinity and sodicity (Grieve et al., 2012; Munns and Tester, 2008; Khan and Gul, 2006).

In saline and sodic soils, seed germination is one of the most important life stages in a plants life cycle (Pujol et al., 2000; Ungar, 1978). Glycophytic and halophytic plants often exhibit delayed germination and reduced final germination rates in response to salinity, with germination in halophytic species reduced primarily by osmotic effects and glycophytic species by ionic effects (Zhang et al., 2012; Dodd and Donovan, 1999). Significant amounts of research, however, indicates that halophytic plants, in general, are more resistant to salinity at this stage of development (Kieffer and Ungar, 1997; Lauchli and Epstein, 1990; Ungar, 1978). Ungar (1978) indicates that halophytic seeds avoid salinity-induced osmotic stress through induced dormancy during periods in which high salt concentrations are present in the topsoil. In contrast to the seed of most glycophytes, halophyte seeds can remain dormant for a number of years while maintaining their viability, allowing germination to occur during periods of high precipitation when the majority of salts have been leached from the topsoil and optimal growing conditions are present (Kieffer and Ungar, 2002; Ungar, 1978).

At later growth stages, halophytic, and to a lesser degree, glycophytic plant species utilize a number of structural and chemical defense mechanisms which contribute to their overall tolerance to salinity-induced stress. Structural traits exhibited by halophytes such as glands, bladders, and salt hairs allow these plants to excrete excess salts when salt concentrations begin to reach toxic levels in their tissues (Grieve et al., 2012; Hasegawa et al., 2000; Glenn et al., 1999; Ungar, 1998). The osmotic imbalance created in saline-sodic soils forces plants to make osmotic adjustments to maintain sufficient water and nutrient uptake (Manouski and Kaleogerakis, 2012; Hasegawa et al., 2000; Lauchli and Epstein, 1990). In halophytic species, osmotic adjustments are achieved through the uptake and subsequent storage of Na in the vacuoles of mature leaf tissue and by the production of organic acids, sugars, soluble solids, and proteins which regulate osmotic processes within the plant (Grieve et al., 2012; Flowers and Colmer, 2008, Ashraf and Harris, 2004). Similarly, glycophytes produce significant concentrations of these organic compounds in an attempt to achieve osmotic homeostasis, however, the concentrations produced are often not enough to sufficiently alter osmotic gradients in highly saline soils. (Flowers and Colmer, 2008; Hasegawa et al., 2000). Furthermore, glycophytes are incapable of compartmentalizing Na and Cl in plant tissues and, conversely, avoid its adsorption through stomatal closure, which reduces transpiration and subsequent water uptake (Chaves et al., 2009; Hasegawa et al., 2000). Salt exclusion is a short-term defense mechanism for osmotic stress, as it results in the decrease of photosynthetic activity which reduces plant growth and function (Munns and Tester, 2008). Comparatively, the ability of halophytic plant species to resist stressors induced by salinity through salt exclusion and efficient osmotic regulation gives them significant potential for revegetation activities on brine-contaminated soils, while the various defense mechanisms of glycophytes are often insufficient to sustain growth in these conditions (Vavrek et al., 2004).

The Effects of Brine on Biotic Systems

Soil biology including various species of fungi, bacteria, nematodes, and other microbes can be negatively impacted by both direct and indirect effects of brine releases. For example, Sublette et al. (2007) discovered an average reduction in phospholipid fatty acid (PLFA) concentrations, a measure of microbial biomass, of approximately 50% in brine-impacted soils. Similarly, Rhykerd et al. (1995) found a decrease in microbial activity and CO_2 production from soils contaminated with brines at increasing level of EC. The primary direct effect of salts on microbial communities in the soil occurs through the induction of osmotic stress, which reduces microbial metabolic activity and results in the mortality of many species (Chowdhury et al., 2011). Indirect effects of salinity on soil biology include the loss of vegetation following a spill, which over time reduces the organic matter required by organisms for metabolic processes (Sublette et al., 2007).

Brine spills may also have significant effects on aquatic and terrestrial biota. In a study of brine spills across the states of Pennsylvania, New Mexico, Colorado, and North Dakota, Maloney et al. (2017) estimated that brine spills in these states occurred at an average distance of 580 m away from streams, causing brine releases to be particularly hazardous to the health of aquatic ecosystems. In a study testing the effects of major ionic constituents most commonly found in brine (i.e. Na, Cl, K, Ca) on aquatic organisms, Wang et al. (2019) found that over a period of 7-d, the survival and growth of fathead minnow (*Pimephales promelas*) and fatmucket (*Lampsilis siliquoidea*) were significantly decreased at salt concentrations of 4X and 2X reference conditions, respectively, following a brine spill near Blacktail Creek, ND. In terrestrial environments, Efroymson et al. (2004) suggested the deleterious effects of brine and hydrocarbon spills on habitat quality may harm vertebrates more than the potential for direct toxicity and, over time, may result in population declines and decreased species richness.

Remediation of Brine-Contaminated Land

Factors Influencing Remediation

The deleterious effects of oil-field brine to soil and plant health often persist for some time following spill incidents and, due to the solubility of NaCl (360 g L^{-1} at 25°C) (Haynes, 2014), contamination can spread quickly to adjacent areas. The simultaneous reduction in agricultural productivity, surface/ground water quality, and ecosystem services of contaminated land often requires that the soils of these sites be remediated, and vegetation be restored in some capacity. Remediation of brine-contaminated land is attempted utilizing a variety of in-situ or ex-situ methods. The choice of remediation method is based on site characteristics, the cost-effectiveness of inputs, and the potential for contamination to migrate to land and water resources adjacent to the site (Sublette et al., 2007; Harris et al., 2005). Important site characteristics that determine the applicability of remediation methods include the severity of contamination, soil texture, drainage capability, depth of contamination, depth to ground water, the topography of the site, and the prevailing climatic conditions (Qadir et al., 2007; Harris et al., 2005; Vavrek et al., 2004; Qadir et al., 2000). In addition to the characteristics of the site, the cost-effectiveness of various methods is governed by the remediation goals established between landowners and industry personnel in conjunction with the approval of plans by government agencies (ND DOH, 2016). In cases where contamination has the potential to migrate to adjacent land and water resources, government agencies may require additional steps to be taken to mitigate and contain the effects of the spill (ND DOH, 2016).

Ex-Situ Remediation

Ex-situ remediation techniques involve the mechanical excavation of contaminated soil and its transportation to an offsite location for treatment or disposal (Kuppusamy et al., 2016; Newell, 2006; Harris et al., 2005). The most prevalent ex-situ remediation method used for brine-contaminated soils consists of the excavation and disposal of impacted soils and vegetation. Excavation and removal, which is commonly referred to as "dig and haul" within the Williston Basin, is used for impacted sites that are extremely contaminated with salts, situated near important water resources, or incompatible with in-situ remediation methods (Sanchez, 2017; Gleason et al., 2014; Harris et al., 2005). Following excavation, contaminated soil is disposed of in landfills which have been pre-approved by state agency officials (ND DOH, 2016; Young et al., 2011). Soil that has been removed from the spill site is often replaced with locally sourced topsoil exhibiting similar, pre-disturbance, physical and chemical properties (Derby et al., 2016).

Another form of ex-situ remediation that has been used for brine-impacted soils is soil washing or scrubbing. The washing of excavated soil occurs in a separation unit which utilizes aqueous solutions composed of either fresh or brackish water in conjunction with various chemical amendments to remove Na from soil exchange sites (Kuppusamy et al., 2016). Following the washing process, soil can then be placed back in its original location. The use of ex-situ remediation techniques provides stakeholders with an expedient and efficient means to mitigate or remove the harmful effects of brine-contamination to soils. However, the financial costs associated with these methods, \$154 Mg^{-1} (Kuppusamy et al., 2016) for soil washing and

$1632 Mg^{-1} (Dustin Anderson, personal communication, 2018) for dig and haul, often makes them far more expensive than other methods of remediation (Gleason et al., 2014; Harris et al., 2005). While being the most prevalent remediation technique used in the Williston Basin due to its expediency, the dig and haul method requires the use of heavy equipment and the construction of transportation infrastructure, which may cause damage to adjacent, non-contaminated soils through compaction and vegetation removal. Furthermore, the removal of native topsoil only displaces the contamination problem to specially constructed landfills, where the space for copious amounts of soil may be limited (Young et al., 2011). A final limitation to this method is the scarcity of high-quality replacement soil in the region.

In-Situ Remediation

Natural Attenuation

In-situ remediation consists of treating brine contamination onsite with the native soils left in place (Kuppusamy et al., 2016). Natural attenuation, a passive, or hands-off form of in-situ remediation, relies on natural precipitation and drainage regimes to leach salts out of the topsoil, allowing for subsequent revegetation of the site and the recovery of soil function (Leskiw et al., 2012; Auchmoody and Walters, 1988). The capability of brine-contaminated sites to recover through natural attenuation has received little attention in the literature, however, factors including climate, soil texture, and water table depth have been identified as the primary determinants for the successful use of this method (Leskiw et al., 2012). In their analysis of a brine spill site in British Columbia, Leskiw et al. (2012) found that over a period of eight years, annual precipitation amounts were adequate to significantly leach brine salts from a sandy loam topsoil and clay loam subsoil. In northwestern Pennsylvania, Auchmoody and Walters (1988) concluded that high amounts of precipitation in the study area during a four-year period was able to sufficiently remove salts from a silt loam soil and allowed for the re-establishment of vegetation. Alternatively, natural attenuation of brine-contaminated soils in semi-arid and arid regions may be limited due to the lack of precipitation for leaching, prevalence of fine-textured soils, and the high concentrations of salts found in brines produced in the region (Kieffer and Ungar, 2001; Murphy et al., 1988). In their study of an abandoned brine disposal pit in North Dakota, Murphy et al. (1988) found that little dilution of salts had occurred over a 10 yr period and estimated that salt concentrations at this site would remain high for decades or even centuries without active remediation.

Soil Amendments and Leaching

The active, in-situ remediation of brine-contaminated soils, in a majority of cases reported in the literature, is attempted through the use of a combination of soil amendments, irrigation, and drainage (Chaganti and Crohn, 2015; Qadir et al., 2014; Bahceci, 2009; Harris et al., 2005; Vavrek et al., 2004; Qadir et al., 2003; Artiola et al., 2000; Atalay et al., 1999; Ashworth and Crepin, 1999; Dejong, 1982). Soil amendments are often classified as either chemical or organic, with the choice of amendment(s) determined by their availability, cost, and effectiveness in improving soil physical, hydraulic, and edaphic properties (Chaganti and Crohn, 2015; Vavrek et al., 2004; Atalay, 1999). In the remediation of sodic and saline-sodic soils, chemical amendments provide a source of divalent cations such as Ca which aid in the displacement of Na from soil exchange sites and help promote the aggregation of soil particles, thereby improving the ability of water to move through the soil profile (Vavrek et al., 2004; Dejong, 1982). Gypsum ($CaSO_4•H_2O$), has traditionally been employed as the primary chemical amendment for ameliorating the effects of sodic soils (Sanchez, 2017; Oster et al., 1999). Although gypsum exhibits a relatively low solubility in water (2.1-2.6 g L^{-1}), it provides a significant amount of Ca for the mobilization of Na in the soil and, in low EC soils, provides enough electrolytes to increase the EC of the soil solution and promote a state of flocculation between clay particles (Artiola et al., 2000; Shainberg and Letey, 1984; Dejong, 1982). In an experiment comparing the Na removal efficiencies of $CaSO_4$, $CaCl_2$ and organic (manure, *Medicago sativa*, and *Sorghum bicolor*) treatments, Robbins (1986) found that gypsum provided the most significant increase in Na removal efficiency.

The gypsum requirement (Mg ha^{-1}) for Na-impacted soils can be calculated using a variety of different formulas available in the literature. However, significant variation is often found between the values calculated using these equations (Ashworth and Crepin, 1999; Oster et al., 1999). A commonly used equation to determine the gypsum requirement of sodic soils was developed by Oster et al. (1999) and is based on the initial and desired (final) exchangeable sodium percentage (ESP) of the soil:

$$GR = 0.86FD\sigma_b(CEC)(ESP_i - ESP_f)/100 \; [1]$$

GR= gypsum requirement (Mg ha^{-1})

F= 1.3 or 1.1 for ESP_f of 5 or 15%, respectively

D= soil depth (m)

σ_d= soil bulk density (Mg $(m^3)^{-1}$)

CEC= cation exchange capacity ($mmol_c$ kg^{-1})

ESP_i, ESP_f= initial and final exchangeable sodium percentage, respectively.

Other chemical amendments including $CaCO_3$, $CaCl_2$, $Ca(NO_3)_2$, $MgSO_4$, $MgCl_2$, and H_2SO_4 have also been used in research applications to reclaim sodic and saline-sodic soils with varying amounts of success (Artiola et al., 2000; Atalay et al., 1999; Merrill et al., 1990; Clark and Thimm, 1975; Prather et al., 1978). An app for iOS and Android mobile devices has been developed by North Dakota State University that can be used to calculate GR, just search "gypsum requirement" in the app store.

The application of organic amendments, in conjunction with chemical amendments, to brine-contaminated soils has been shown to provide several benefits that aid in the successful remediation of brine spill sites. Commonly used organic amendments include straw, wood chips, hay, composted livestock manure, food processing wastes, green manure, biochar, and humates such as leonardite (Zhang et al., 2008; Sublette et al., 2007; Vavrek, 2004; Conway, 2001; Barzegar et al., 1997). In general, organic amendments improve soil structure, enhance the growth and activity of microbial communities, increase percolation and infiltration rates of the soil, and decrease water loss to evaporation from the soil surface (Zhang et al., 2008; Sublette et al., 2007; Vavrek, 2004; Conway, 2001; Barzegar et al., 1997). In their work remediating a brine spill site in Oklahoma, Harris et al. (2005) found that the application of a thick layer of native hay in combination with an artificial subsurface drainage system was effective in maintaining soil permeability, reducing evaporation from the soil surface, and removing significant concentrations of Na and Cl from the soil. Barzegar et al. (1997) found that the addition of pea straw to soils at increasing levels of sodicity had a positive influence on the structural stability of the soil and could aid in the removal of Na from salt-affected soils.

Conventional in-situ remediation techniques require sufficient volumes of water to leach salts out of the topsoil (Young et al., 2011; Bahceci, 2009; Qadir et al., 2000). The need for sometimes large amounts of water is often confounded by the lack of precipitation in arid and semi-arid environments (Bahceci, 2009; Keiffer and Ungar, 2002). In these conditions, irrigation is often required to supplement natural precipitation. For saline soils, Qadir et al. (2000) identified three irrigation techniques (continuous ponding, intermittent ponding, and sprinkling) that are commonly used to leach salts out of the topsoil. The leaching efficiency of these three methods had been tested previously by Oster et al. (1972) and were found to decrease in the following order: intermittent ponding, sprinkling, and continuous ponding.

The amount of time and volume of water needed to leach salts from brine-impacted soils depends on the depth to be remediated, the soil texture, soil amendments applied, the quality of irrigation water, and the prevailing climatic conditions (Bahceci, 2009; Oster et al., 1999; Shainberg and Letey, 1984). For brine-contaminated soils, various estimates concerning the amount of time and water needed for sufficient leaching of Na have been given by a number of authors in the literature. For example, Jury and Weeks (1978) estimated approximately 31 pore volumes of a saturated gypsum solution would be needed to leach Na from a fine-textured soil, while Munn and Stewart (1989) estimated that a 100-fold dilution of freshwater was necessary to decrease salt concentrations of a brine-contaminated soil in Ohio to levels in which crop species would be able to survive. Using Hydrus 1-D software to model solute travel times of brine through a homogenous, silt loam soil under continuous ponding conditions of freshwater, Klaustermeier (2016) indicated that a prohibitive amount of time would be needed to completely remove Na from a 150 cm profile. These studies suggest that significant amounts of time and water would need to be applied to sufficiently leach salts from the topsoil.

In addition to the need for adequate volumes of water for leaching, soil drainage is an important factor that can determine the effectiveness of this remediation method (Conway, 2001; Qadir et al., 2000). For leaching to be effective, salts must be transported to a significant depth in the subsoil to reduce the risk of capillary rise or be translocated to a natural or manmade pour point where it can be collected and removed. Limiting factors for soil drainage include the presence of a high water table, impermeable subsoil layers, and reduced infiltration/permeability rates of the topsoil caused by swelling and dispersion of clay particles (Bahceci, 2009; Harris et al., 2005; Vavrek et al., 2004; Oster, 2001). In situations where high water tables or impermeable subsoil layers are present, artificial subsurface drainage may be used to lower water table depths and collect the leachate from the topsoil for disposal (Derby et al., 2016; He et al., 2015; Young et al., 2011; Harris et al., 2005).

The use of this remediation strategy in semi-arid environments can often produce mixed results, while in most situations, incurring significant costs to stakeholders. Gypsum, for example, has traditionally been the most common amendment used to reduce the harmful effects of Na in the soil profile, yet its' low solubility causes it to only be effective to the depth at which it is applied, which in most cases is not to the entire depth of soil contamination (Sublette et al., 2007; Harris et al., 2005; Qadir, 2000; Artiola, 1999; Ilyas, 1997; Robbins, 1986). In addition to this limitation, a significant amount of irrigation water and time is needed to leach salts from these soils, even with the addition of amendments (Kieffer and Ungar, 2001; Munn and Stewart, 1989; Jury and Weeks, 1978). With the increase in freshwater water use for oil development and the continued need for agricultural irrigation, competition for the sometimes scarce water resources of the region may limit the water availability for remediation purposes (NDSWC, 2016). If sufficient water resources can be found, drainage may also become an issue for many brine spill sites. The presence of high water tables, fine-textured soils with low infiltration rates and permeabilities, and impermeable subsurface layers have been found to be the main determinants of remediation failure or success when using leaching to remove Na from the soil profile (Harris et al., 2005; Vavrek, 2004; Oster et al., 2001; Qadir et al., 2000). When these conditions are found, the installation of subsurface tile drainage has been used to collect the leachate and permanently remove it from the soil profile, however, high installation costs and/or topography may limit this option in some instances (Derby et al., 2016; Young et al., 2011; Harris et al., 2005). A final factor which may limit the long-term success of this methodology for brine spill remediation is the potential for resalinization of the topsoil through capillary rise of groundwater and dissolved solutes (Derby et al., 2016; Thimm, 1990).

Phytoremediation

Phytoremediation, also referred to as phytoextraction, is the use of growing vegetation to ameliorate the effects of various pollutants found in environment (Manouski and Kalogerakis, 2011). Phytoremediation has been identified as a potential method for the remediation of brine-impacted soils in oil producing regions, although a limited amount of research has been devoted to its efficacy in the Williston Basin (Young et al., 2011; Manouski and Kalogerakis, 2011; Keiffer and Ungar, 2002; Keiffer and Ungar, 2001). In some situations, phytoremediation utilizes halophytic (salt-tolerant) plants that are capable of completing their lifecycles in soils exhibiting EC values upwards of 20 dS m^{-1} (Flowers et al., 2010; Keiffer and Ungar, 2002; Keiffer and Ungar, 2001). The establishment of halophytes stabilizes salt-affected soils and promotes the removal of NaCl through direct uptake and improvement of soil structure and chemistry (Qadir et al., 2007).

In sodic and saline-sodic soils, various halophytes have been shown to accumulate significant amounts of Na in the vacuoles of leaf and stem tissues in an effort to maintain the osmotic gradient between the soil solution and the plant (Flowers and Colmer, 2008; Grieve et al., 2012; Manouski and Kalogerakis, 2011; Ashraf and Harris, 2004; Ke-Fu et al., 1991). Through the harvest and disposal of the above ground biomass, this process has been used to decrease the overall concentration of Na in the soil profile (Young et al., 2011; Qadir et al., 2007, Qadir et al., 2003; Keiffer and Ungar, 2002; Keiffer and Ungar, 2001; Qadir et al., 2000). For example, Ke-Fu et al. (1991) estimated that through the establishment and harvest of the halophyte species *Suaeda salsa*, approximately 3,090-3,860 kg Na ha^{-1} or 4.5% of total Na could be removed from a saline, medium-textured soil. In their research of brine spill site in Ohio, Keiffer and Ungar (2001) found that the halophyte species *Atriplex prostrata*, *Salicornia europaea*, *Salicornia calceoliformis*, and *Hordeum jubatum* decreased Na concentrations in the soil by 17%, 10%, 10%, and 9%, respectively, over the course of a single growing season.

The establishment of halophytic vegetation has also been proven to enhance several of the physical and hydraulic properties of salt-affected soils. Root systems established by halophytic plants, especially those that protrude deep into the soil profile, provide numerous pathways by which water can move through the soil profile, thus increasing the leaching efficiency of Na and Cl out of the topsoil (Manousaki and Kalogerakis, 2011; Qadir et al., 2003; Qadir et al., 2000; Ilyas et al., 1993). For example, Ilyas et al. (1993) found that the growth of alfalfa roots in a fine-loamy, saline-sodic soil, resulted in an increase of saturated hydraulic conductivity of approximately 258% when used in association with gypsum, allowing for significant reductions in Na and soluble salt concentrations of the upper profile over a one-year period. Plant roots, through the respiration of CO_2, have also been shown to increase the rate of calcite ($CaCO_3$) dissolution in calcareous soils, providing a source of Ca to displace Na from cation exchange sites and flocculate soil particles (Qadir et al., 2007, Qadir et al., 2000). Similarly, microorganisms in the soil increase the partial pressure of CO_2 in the soil profile and produce organic acids that further promote the dissolution of calcite in calcareous-sodic soils (Qadir, 2000).

In comparison to ex-situ methods or the in-situ method of using soil amendments, irrigation, and leaching, phytoremediation has the potential to provide an inexpensive alternative to stakeholders (Young et al., 2011; Manousaki and Kalogerakis, 2011; Qadir et al., 2003). The effectiveness of phytoremediation in brine-impacted soils, however, has received little attention in the literature, particularly in the Williston Basin (Manouski and Kalogerakis, 2011; Young et al., 2011; Keiffer and Ungar, 2002; Keiffer and Ungar, 2001). The lack of information concerning the use of this method in these soils extends to the identification of appropriate halophytic plant species and their tolerance to various contaminants found in oil-field brine (Vavrek et al., 2004). In addition, the time needed for phytoremediation to be effective in brine-impacted soils may prove to be a limiting factor in many situations, as the salt concentrations of these soils are much greater than those found in agricultural settings where this method has been proven to have the most success. Qadir et al. (2007) state that in highly sodic soils, the establishment of halophytic species is often uneven, reducing their effectiveness in promoting the leaching of Na from the soil profile and uptake through above-ground biomass. For example, at a brine spill site in Alberta, Canada, Young et al. (2011) found that there was significant spatial variation in the establishment of the halophyte *Atriplex patula*, with some areas showing little establishment over a three-year period. In addition, salt uptake by halophytes contributes little to their efficiency in reducing Na from the soil profile, indicating that reductions through harvest and removal of above-ground biomass may take decades to be effective, even under optimal growing conditions (Jesus et al., 2015; Qadir, 2007).

Contemporary and Experimental Remediation Methods

Due to the increase in frequency of brine spills over the past decade throughout western North Dakota, an urgent need has been created for alternative methods to expedite and improve the effectiveness of brine spill remediation. Over this time period, several methods have been proposed to fulfill these needs including electrokinetics, crystallization inhibitors, wicking materials, and microbial-assisted phytoremediation. Electrokinetics is a method of in-situ remediation that utilizes electrical fields established in the soil matrix using low intensity direct currents (Acar, 1993). These electrical fields induce the migration of soil contaminants to an anode (positive) or cathode (negative) that have been inserted into the soil profile (Camaselle, 2013). In brine-impacted soils, a phenomenon known as electromigration causes positively charged ions such as Na, Ca, and Mg to migrate towards the cathode and negatively charged ions such as Cl and SO_4 to migrate towards the anode (Athmer et al., 2012). Ion migration also occurs through electro-osmotic, or fluid flow to the cathode, which enhances the accumulation of cations such as Na but limits the absorption of anions such as Cl by the anode. In laboratory studies using electrokinetics to remediate a clay/silt loam soil contaminated with NaCl (1000 mg L^{-1}), Athmer and Wilkens (2013) found Na and Cl concentrations could be reduced by 85% and 65%, respectively. Field scale application of electrokinetics has been conducted at a brine spill site near Williston, North Dakota with results from the first 191 days of operation indicating an average reduction in Cl concentration of approximately 47% (Athmer et al., 2017).

In semi-arid environments where PET is much greater than precipitation, the upward capillary transport of both water and solutes to the soil surface is a common process. This characteristic process of dryland environments often limits the effectiveness of many conventional methods of in-situ remediation such as leaching and contributes to the high costs internalized by various stakeholders. To work with this process rather than against it, Klaustermeier et al. (2017) suggested the use of the crystallization inhibitor hexacyanoferrate ($Fe_4[Fe(CN)_6]_3$) to induce hopper crystal growth of NaCl on the soil surface, which could then be harvested and permanently removed from the soil profile. Conceptually, this method would utilize the evaporative flux established at the soil surface following a brine spill and the capillary rise of soil water to accumulate salts in the upper portions of the soil profile, where the crystallization inhibitor would then induce the growth of NaCl hopper crystals (Klaustermeier et al., 2017). In laboratory experiments utilizing a surficial application of the crystallization inhibitor to NaCl-contaminated sandy loam, loam, and silty clay soils, this method was found to reduce the mass of Na (34.75 g total) in the soil by 0.46, 0.57, and 0.29 g g^{-1} (grams harvested salt at the soil surface per total grams of NaCl applied to the soil), respectively (Klaustermeier et al., 2017). In subsequent experiments, the authors found that the re-application of the crystallization inhibitor following the initial harvest of salts produced little to no additional salt growth, indicating that this method may only be applicable for the partial remediation of brine-impacted soils (Swallow and O'Sullivan, 2019; Klaustermeier et al., 2017). Furthermore, it was found that the effectiveness of the crystallization inhibitor was limited at low salt concentrations (<0.5M NaCl) and produced little efflorescence in the presence of SO_4-based salts (Klaustermeier et al., 2017).

To overcome the limitations confronted by the methodology tested by Klaustermeier et al. (2017), Swallow and O'Sullivan (2019) and Green et al. (2019) suggested the use of highly absorbent "wicking" materials treated with or without the crystallization inhibitor potassium cyanoferrate to remediate brine-impacted soils. Wicking materials contain high amounts of fine- to medium-sized pores which, through capillary suction, can absorb significant volumes of water and dissolved solutes from the soil medium. Highly absorbent materials have previously been applied for several uses including the removal of heavy metals from aqueous solutions (Yu et al., 2018), desalinization of seawater (Hansen et al., 2015), and oil spill clean-up (Adebajo et al., 2003). In part one of their experiment, Swallow and O’Sullivan (2019) used Jiffy-Strips® peat pots that had been treated with 50 mL of 0.01 M potassium ferrocyanide as a wicking medium. Treatments included: 1) a control consisting of surficial application of the crystallization inhibitor and no wick, 2) a wick treated with a crystallization inhibitor connecting the soil and water reservoir, 3) a wick treated with a crystallization inhibitor placed on the soil surface, and 4) a combination of treatments one and two. Following a 14-day incubation period, Na concentrations in treatments one, two, three, and four were reduced by 50, 5, 50, and 81% respectively. In part two of the experiment, the authors used the design of treatment four in part one to test the effectiveness of 0.01 M, 0.005 M, 0.001 M, and 0 M concentrations of the inhibitor over a 30-day incubation period. Of the inhibitor concentrations tested, the 0.01 M solution caused the greatest reduction in Na concentration of approximately 90% (Swallow and O’Sullivan, 2019). Although proven effective in the laboratory, the authors note that field implementation still needs to be conducted to prove its effectiveness in these conditions.

A final experimental method for the remediation of brine-impacted soils that has been proposed for commercial use consists of a form of phytoremediation that utilizes plant growth in association with the synergistic effects of soil microbes to achieve successful contaminant reduction or removal (Gerhardt et al., 2009). A subset of soil microbial communities commonly referred to as plant-growth promoting rhizobacteria (PGPR) have been identified for their potential in soil impacted with salts and heavy metals (Glick, 2010; Glick, 1995). PGPR reduce plant stress by decreasing the levels of the plant hormone ethylene, which is responsible for reducing plant metabolism and growth when osmotic or edaphic stressors, such as high concentrations of salts, are present in the soil (Chang, 2014; Glick, 2010; Cheng et al., 2007; Mayak et al., 2004). Following a brine release, soil microbial communities may experience significant declines in both species richness and density, requiring the isolation and introduction of various strains PGPR to plant seed, often through inoculation or seed coatings (Chang et al., 2014; Cheng et al., 2007; Sublette et al., 2007; Rhykerd et al., 1995). Through the use of seed inoculated with various strains of the bacteria *Psuedomonas putida*, Chang et al. (2014) observed an increase in roots biomass and growth of *Hordeum vulgare* (barley) and *Avena sativa* (oats) in salt-affected soils (EC = 9.4 dS m^{-1}), when compared to the control (non-treated seed), of 200 and 50%, respectively. In field trials located in Saskatchewan, Canada, Chang et al. (2014) also observed enhanced growth rates of treated barley and oats in soils exhibiting EC between 4 and 24 dS m^{-1}. Similarly, Cheng et al. (2007) found that the growth *Brassica napus* (canola) seed inoculated with *Psuedomonas putida* was equal to or greater than the growth of non-treated seed in salt solutions at 10° and 20° C, respectively. Although the use of PGPR in association with phytoremediation has shown promising results, the potential limitations for this method may require additional field-scale trials to be conducted to ascertain this methods effectiveness in other locations.

Conclusions

The immense growth of oil and natural gas production in the Williston Basin has resulted in a significant increase in the number and frequency of brine spills. These spills occur through various pathways including, but not limited to, pipeline leaks and trucking accidents. Due to the high concentrations of dissolved salts found in brine, its release can cause significant impacts to the surrounding environment. The dominant salt species found in brine, NaCl, can cause the deterioration of soil structural and hydraulic properties through processes including swelling, dispersion, surface crusting, hardsetting, and surface sealing. Vegetation is often killed on contact with brine, leaving spill sites barren and susceptible to wind and water erosion. In addition, the growth of new vegetation following a spill is inhibited by poor soil structure, osmotic stress, and ion toxicity. Certain halophytic (salt-tolerant) plant species, however, can survive in highly saline environments through structural and chemical adaptions such as salt glands and bladders, osmotic regulation through the uptake of salts and production of organic solutes in their tissues, and ability to maintain seed viability for as many as four years until edaphic conditions are conducive for germination.

The harmful effects of brine on the environment coupled with the semi-arid climate of the region often necessitates the use of anthropogenic remediation techniques to expedite the removal of contaminants and limit the risk of further contamination to surrounding areas. Remediation of brine contaminated soils is often conducted through ex-situ methods such as excavation and disposal (i.e. dig and haul) or in-situ methods including soil amendment application and leaching. Current remediation methods are associated with high costs to stakeholders and often achieve only partial or short-term amelioration of contaminated soils. To confront the expanding issue of brine contamination and reduce the time and financial resources needed for remediation, several novel remediation techniques have been proposed including the use of plant growth promoting rhizobacteria, electrokinetics, crystallization inhibitors, and wicking materials in combination with crystallization inhibitors. These methods have been shown to be relatively effective in removing NaCl from contaminated soils in laboratory settings, however, further research in field trials needs to be conducted before these methods can be efficiently used at a commercial scale.

References

Acar, Y.B. and A.N. Alshawabkeh. 1993. Principles of electrokinetic remediation. Environ. Sci. Tech. 27: 2638-2647.

Adebajo, M.O., R.L. Frost, J.T. Kloprogge, O. Carmody and S. Kokot. 2003. Porous materials for oil spill cleanup: a review of synthesis and absorbing properties. J. Porous Mater. 10: 159-170.

Anderson, S.B. and W.P. Eastwood. 1968. Natural gas in North Dakota. Am. Assoc. Pet. Geol. North Dakota Geological Survey. 2: 9

Artiola, J.F., H. Gebrekidan and D.J. Carty. 2000. Use of langbeinite to reclaim sodic and saline sodic soils. Commun. Soil Sci. Plant Anal. 31: 2829-2842.

Aschenbach, T.A. and K. Kindscher. 2006. Plant species on salt-affected soil at Cheyenne Bottoms, Kansas. Trans. Kans. Acad. of Sci. 109: 207-213.Ashraf, M. and P. Harris. 2004. Potential biochemical indicators of salinity tolerance in plants. Plant Sci. 166: 3-16.

Ashraf, M. and M.R. Foolad. 2005. Pre-sowing seed treatment-a shotgun approach to improve germination, plant growth, and crop yield under saline and non-saline conditions. Adv. Agron. 88, 223–271. Doi: 10.1016/S0065-2113(05)88006-X.

Ashraf, M. and P. Harris. 2004. Potential biochemical indicators of salinity tolerance in plants. Plant Sci. 166: 3-16.

Ashworth, J., D. Keyes and J.-M. Crépin. 1999. A comparison of methods for gypsum requirement of brine-contaminated soils. Can. J. Soil Sci. 79: 449-455.

Atalay, A., T. Pyle and R. Lynch. 1999. Strategy for restoration of brine-disturbed land. J. Soil Cont. 8: 307-328.

Athmer, C.J., Huntsman, B.E., and D. Andersen. 2017. Implementation of electrokinetic based soil desalinization: year 2 update. Presentation.

Athmer, C. J., and R. J. Wilkens. 2013. Desalinization of Field Soil Using Radial Electromigration and Electroosmosis. J. Hazard., Toxic, and Radioact. Waste, 18(1): 83-86.

Athmer, C., Ruef, C., Jones, T. J., and R. J Wilkens. 2012. Desalinization of kaolin soil using radial electromigration and electroosmosis. J. Hazard., Toxic, and Radioact. Waste, 17(1): 16-20.

Auchmoody, L. and R. Walters. 1988. Revegetation of a brine-killed forest site. Soil Sci. Soc. Am. J. 52: 277-280.

Bader, J.W. 2016. The Dakota Group of the Williston Basin: An Important Geologic Unit for Produced Water from Oil and Gas Development in North Dakota. Available online at https://www.dmr.nd.gov/ndgs/documents/newsletter/2016Winter (verified 11 Nov. 2018).

Bahceci, I. 2009. Determination of salt leaching and gypsum requirements with field tests of saline–sodic soils in central Turkey. Irrig. and Drain.: J. Int. Comm. Irrig. and Drain. 58: 332-345.

Barzegar, A.R., P.N. Nelson, J.M. Oades and P. Rengasamy. 1997. Organic matter, sodicity, and clay type: Influence on soil aggregation. Soil Sci. Soc. Am. J. 61: 1131-1137.

Blondes, M. S., K. D. Gans, M. A. Engle, Y. K. Kharaka, M. E. Reidy, V. Saraswathula, J. J. Thordsen, E. L. Rowan, and E. A. Morrissey. 2017. U.S. Geological Survey National Produced Waters Geochemical Database v2. 3 (PROVISIONAL). U.S. Geological Survey: U.S. Geological Survey, Eastern Energy Resources Science Center, Reston, VA, U.S.A. Available at https://energy.usgs.gov/EnvironmentalAspects/EnvironmentalAspectsofEnergyProductionandUse/ProducedWaters.aspx#3822349-data. Verified 14 April 2019.

Bluemle, J.P. 2016. North Dakota's Geological Legacy: Our Land and how it Formed. North Dakota State University Press, Fargo, North Dakota.

Breit, G.N., and J.K Otton. 2002. USGS produced waters database: U.S. Department of the Interior, United States Geological Survey.

Cameselle, C., R.A. Chirakkara and K.R. Reddy. 2013. Electrokinetic-enhanced phytoremediation of soils: status and opportunities. Chemosphere 93: 626-636.

Chaganti, V.N. and D.M. Crohn. 2015. Evaluating the relative contribution of physiochemical and biological factors in ameliorating a saline–sodic soil amended with composts and biochar and leached with reclaimed water. Geoderma 259: 45-55.

Chang, P., K.E. Gerhardt, X.-D. Huang, X.-M. Yu, B.R. Glick, P.D. Gerwing, and B.M. Greenberg. 2014. Plant growth-promoting bacteria facilitate the growth of barley and oats in salt-impacted soil: implications for phytoremediation of saline soils. Int. J Phytorem. 16: 1133-1147.

Chaves, M.M., J. Flexas, and C. Pinheiro. 2009. Photosynthesis under drought and salt stress: regulation mechanisms from whole plant to cell. Ann. Bot. 103: 551-560.

Cheng, Z., E. Park and B.R. Glick. 2007. 1-Aminocyclopropane-1-carboxylate deaminase from Pseudomonas putida UW4 facilitates the growth of canola in the presence of salt. Can. J. Microbiol. 53: 912-918.

Chowdhury, N., P. Marschner and R. Burns. 2011. Response of microbial activity and community structure to decreasing soil osmotic and matric potential. Plant and Soil 344: 241-254.

Clark, C. and J. Veil. 2009. Produced water volumes and management practices in the United States. Argonne National Lab, Argonne, IL, United States.

Clark, G. J. and H. F. Thimm. 1975. The reclamation of land affected by oil field brines- Two case histories. Proc. Conf. on the Environ. Effects of oil and salt water on land. Alberta Environment, Edmonton, Alta. 26-36.

Conway, T. 2001. Plant materials and techniques for brine site reclamation. U.S. Department of Agriculture. Plant materials technical note no. 26.

Cozzarelli, I.M., K.J. Skalak, D.B. Kent, M.A. Engle, A. Benthem, A.C. Mumford, K. Haase, A. Farage, D. Harper, S.C. Nagel, L.R. Iwanowisz, W.H. Orem, D.M. Akob, J.B. Jaeschke, J. Galloway, M. Kohler, D.L. Stoliker, and G.D. Jolly. 2017. Environmental signatures and effects of an oil and gas wastewater spill in the Williston Basin, North Dakota. Sci. Tot. Environ. 579: 1781-1793.

Deans, W.S., L.R. Scherer and J. Pulley. 1991. A Study of Horizontal Drilling and the Bakken Formation Williston Basin, North Dakota. North Dakota Geological Survey.

DeJong, E. 1982. Reclamation of soils contaminated by sodium chloride. Can. J. Soil Sci. 62: 351-364.

Derby, N.E., F.X. Casey and T.M. DeSutter. 2016. Effects of oil field brine wastewater on saturated hydraulic conductivity of smectitic loam soils. Can. J. Soil Sci. 96: 496-503.

Dodd, G.L. and L.A. Donovan. 1999. Water potential and ionic effects on germination and seedling growth of two cold desert shrubs. Amer. J. Bot. 86, 1146–1153.

Durham, L.S., 2010, Bakken fractures yield the goods, oil shale takes turn in spotlight: American Association of Petroleum Geologists Explorer, v. 31, p. 34–36. Available at http://www.aapg.org/explorer/2010/10oct/index.cfm. Verified 11 November 2018.

Efroymson, R.A., T.M. Carlsen, H.I. Jager, T. Kostova, E.A. Carr, W.W. Hargrove, J. Kercher, and T.L. Ashwood. 2004. Toward an ecological framework for assessing risk to vertebrate populations from brine and petroleum spills at exploration and production sites. Landscape Ecology and Wildlife Habitat Evaluation: Critical Information for Ecological Risk Assessment, Land-Use Management Activities, and Biodiversity Enhancement. ASTM International. Doi: 10.1520/STP11953S

Flowers, T.J. and T.D. Colmer. 2008. Salinity tolerance in halophytes. New Phytol. 179: 945-963.

Flowers, T.J., H.K. Galal and L. Bromham. 2010. Evolution of halophytes: multiple origins of salt tolerance in land plants. Funct. Plant Biol. 37: 604-612.

Franzen, D. and H. Bu. 2018. North Dakota Clay Mineralogy Impacts Crop Potassium Nutrition and Tillage Systems.

Gaswirth, S.B., K.R. Marra, T.A. Cook, R.R. Charpentier, D.L. Gautier, D.K. Higley, T.R. Klett, M.D. Lewan, P.G. Lillis, C.J. Schenk, M.E. Tennyson, and K.J. Whidden. 2013. Assessment of undiscovered oil resources in the bakken and three forks formations, Williston Basin Province, Montana, North Dakota, and South Dakota, 2013. U.S. Geological Survey Fact Sheet 3013.

Gerhard, L.C., S.B. Anderson, and D.W. Fischer. 1990. Petroleum geology of the Williston Basin. Interior cratonic basins. AAPG Memoir 51: 507-559.

Gerhardt, K.E., X.-D. Huang, B.R. Glick and B.M. Greenberg. 2009. Phytoremediation and rhizoremediation of organic soil contaminants: potential and challenges. Plant Sci. 176: 20-30.

Gleason, R.A., T.L.C. Chesley-Preston, J.L. Coleman Jr., S.S. Haines, K.E. Jenni, T.L. Nieman, Z.E. Peterman, M.P. van der Burg, T.M. Preston, B.D. Smith, B.A. Tangen, and J.N. Thamke. 2014. Brine contamination to aquatic resources from oil and gas development in the Williston Basin, United States. No. 2014-5017. U.S. Geological Survey. doi:10.3133/sir20145017

Glenn, E.P., J.J. Brown and E. Blumwald. 1999. Salt tolerance and crop potential of halophytes. Crit. Rev. Plant Sci. 18: 227-255.

Glick, B.R. 2010. Using soil bacteria to facilitate phytoremediation. Biotechnol. Adv. 28: 367-374.

Glick, B.R. 1995. The enhancement of plant growth by free-living bacteria. Can. J. Microbiol. 41: 109-117.

Goldberg, S., I. Lebron, and D. Suarez. 2000. Soil colloidal behavior. In “Handbook of soil science”. M.E. Sumner. CRC Press: New York, NY.

Grattan, S. and C. Grieve. 1998. Salinity–mineral nutrient relations in horticultural crops. Sci. Hortic. 78: 127-157.

Green, A.W., T.M. DeSutter, A.L. Daigh and M.A. Meehan. 2019. Wicking Salts from Brine-Contaminated Soils: A Potential Method for In Situ Remediation. Agric. Environ. Lett. 4(1). Doi: doi:10.2134/ael2018.12.0069

Gregory, K.B., R.D. Vidic and D.A. Dzombak. 2011. Water management challenges associated with the production of shale gas by hydraulic fracturing. Elem. 7: 181-186.

Grieve, C.M., S.R. Grattan and E.V. Maas. 2012. Plant salt tolerance. Agric. Salinity Assess. and Manage. 2: 405-459.

Guerra, K., K. Dahm and S. Dundorf. 2011. Oil and gas produced water management and beneficial use in the Western United States. U.S. Department of the Interior, Bureau of Reclamation.

Hanor, J.S. 2007. Variation in the composition and partitioning of adsorbed cations at a brine-contaminated crude oil production facility in southeastern Louisiana, USA. Appl. Geochem. 22: 2115-2124.

Hansen, R.S., C.S. Narayanan and K.K. Murugavel. 2015. Performance analysis on inclined solar still with different new wick materials and wire mesh. Desalin. 358: 1-8.

Harris, T.M., J.T. Bryan and K.L. Sublette. 2005. Remediation of oil-field brine-impacted soil using a subsurface drainage system and hay. Environ. Geosci. 12: 101-113.

Hasegawa, P.M., R.A. Bressan, J.-K. Zhu and H.J. Bohnert. 2000. Plant cellular and molecular responses to high salinity. Ann. Rev. Plant Biol. 51: 463-499.

Haynes, W.M. 2014. CRC Handbook of chemistry and physics. CRC press.

He, Y., T. DeSutter, F. Casey, D. Clay, D. Franzen and D. Steele. 2015. Field capacity water as influenced by Na and EC: Implications for subsurface drainage. Geoderma 245: 83-88.

He, Y., DeSutter, T. M., and D.E. Clay. 2013. Dispersion of pure clay minerals as influenced by calcium/magnesium ratios, sodium adsorption ratio, and electrical conductivity. Soil Sci. Soc. Am. J. 77(6): 2014-2019.

Iampen, H.T. 2003. The Genesis and Evolution of Pre-Mississippian Brines in the Williston Basin, Canada-USA. M.S. Thesis. University of Alberta, Edmonton.

Iampen, H. T., and B.J. Rostron. 2000. Hydrogeochemistry of pre-Mississippian brines, Williston Basin, Canada–USA. J. Geochem. Explor. 69: 29-35.

Ibrahim, E. A. 2016. Seed priming to alleviate salinity stress in germinating seeds. J. Plant Physiol. 192: 38-46.

Ilyas, M., R. Qureshi and M. Qadir. 1997. Chemical changes in a saline-sodic soil after gypsum application and cropping. Soil Tech. 10: 247-260.

Jambhekar, V., R. Helmig, N. Schröder and N. Shokri. 2015. Free-flow–porous-media coupling for evaporation-driven transport and precipitation of salt in soil. Transp. Porous Media 110: 251-280.

Jensen, G.K.S. 2007. Fluid flow and geochemistry of the Mississippian aquifers in the Williston Basin, Canada-USA: M.S. thesis. Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton.

Jesus, J.M., A.S. Danko, A. Fiúza and M.-T. Borges. 2015. Phytoremediation of salt-affected soils: a review of processes, applicability, and the impact of climate change. Environ. Sci. Pollut. Res. 22: 6511-6525.

Jury, W. and L. Weeks. 1978. Solute Travel-time estimates for tile-drained fields: III. removal of a geothermal brine spill from soil by leaching. Soil Sci. Soc. Am. J. 42: 679-684.

Ke-Fu, Z. 1991. Desalinization of saline soils by Suaeda salsa. Plant and soil 135: 303-305.

Keiffer, C.H. and I.A. Ungar. 2002. Germination and establishment of halophytes on brine-affected soils. J. Appl. Ecol. 39: 402-415.

Keiffer, C.H. and I.A. Ungar. 2001. The effect of competition and edaphic conditions on the establishment of halophytes on brine effected soils. Wetlands Ecol. and Manage. 9: 469-481.

Keiffer, C.H. and I.A. Ungar. 1997. The effect of extended exposure to hypersaline conditions on the germination of five inland halophyte species. Am. J. Bot. 84: 104-111.

Khan, M.A. and B. Gul. 2006. Ecophysiology of high salinity tolerant plants. Halophyte seed germination. 11-30.

Kharaka, Y.K., J.J. Thordsen, E. Kakouros and W.N. Herkelrath. 2005. Impacts of petroleum production on ground and surface waters: Results from the Osage–Skiatook Petroleum Environmental Research A site, Osage County, Oklahoma. Environ. Geosci. 12: 127-138.

Klaustermeier, A.W. 2016. Brine-Contaminated Soils in Western North Dakota: Site Assessment Methodology and a New In-Situ Remediation Method. M.S. thesis. North Dakota State University, Fargo, North Dakota.

Klaustermeier, A.W., A.L. Daigh, R.F. Limb and K. Sedivec. 2017. Crystallization inhibitors and their remediation potential on brine-contaminated soils. Vadose Zone J. 16.

Kondash, A.J., E. Albright and A. Vengosh. 2017. Quantity of flowback and produced waters from unconventional oil and gas exploration. Sci. Tot. Environ. 574: 314-321.

Kuppusamy, S., T. Palanisami, M. Megharaj, K. Venkateswarlu and R. Naidu. 2016. Ex-situ remediation technologies for environmental pollutants: a critical perspective. Rev. Environ. Contam. Toxicol. 236: 117-192.

Kurz, B.A. 2016. A Review of Bakken Water Management Practices and Potential Outlook. EERC, University of North Dakota, Grand Forks, North Dakota.

Lauer, N.E., J.S. Harkness and A. Vengosh. 2016. Brine spills associated with unconventional oil development in North Dakota. Environ. Sci. Technol. 50: 5389-5397.

LeFever, J.A. 1991. History of oil production from the Bakken Formation, North Dakota. North Dakota Geological Survey.

Leskiw, L.A., R.B. Sedor, C.M. Welsh and T.B. Zeleke. 2012. Soil and vegetation recovery after a well blowout and salt water release in northeastern British Columbia. Can. J. Soil Sci. 92: 179-190.

Läuchli, A. and E. Epstein. 1990. Plant responses to saline and sodic conditions. Agric. Salinity Assess. Manage. 71: 113-137.

Maloney, K. O., S. Baruch-Mordo, L.A. Patterson, J.P. Nicot, S.A. Entrekin, J.E. Fargione, J.M. Kiesecker, J.N. Ryan, A.M. Trainor, J.E. Saiers, and H.J. Wiseman. 2017. Unconventional oil and gas spills: Materials, volumes, and risks to surface waters in four states of the US. Sci. Tot. Environ. 581: 369-377.

Manousaki, E. and N. Kalogerakis. 2011. Halophytes—an emerging trend in phytoremediation. Int. J. Phytorem. 13: 959-969.

Marchuk, A. and P. Rengasamy. 2011. Clay behaviour in suspension is related to the ionicity of clay–cation bonds. Appl. Clay Sci. 53: 754-759.

Mayak, S., T. Tirosh and B.R. Glick. 2004. Plant growth-promoting bacteria confer resistance in tomato plants to salt stress. Plant Physiol. and Biochem. 42: 565-572.

McNally, M.S. and A.R. Brandt. 2015. The productivity and potential future recovery of the Bakken formation of North Dakota. J. Unconv. Oil Gas Resour. 11: 11-18.

Merrill, S., K. Lang and E. Doll. 1990. Contamination of soil with oilfield brine and reclamation with calcium chloride. Soil Sci. 150: 469-475.

Mullins, C. E., MacLeod, D. A., Northcote, K. H., Tisdall, J. M., and I.M. Young. 1990. Hardsetting soils: behavior, occurrence, and management. Adv. Soil Sci. 11: 37-108.

Munn, D.A. and R. Stewart. 1989. Effect of oil well brine on germination and seedling growth of several crops. Ohio J. Sci. 89(4): 92-94.

Munns, R. and M. Tester. 2008. Mechanisms of salinity tolerance. Annu. Rev. Plant Biol. 59: 651-681.

Murphy, E.C., A.E. Kehew, G.H. Groenewold and W.A. Beal. 1988. Leachate generated by an oil-and-gas brine pond site in North Dakota. Groundwater 26: 31-38.

Newell, C. and J. Connor. 2006. Strategies for Addressing Salt Impacts of Produced Water Releases to Plants Soil, and Groundwater. American Petroleum Institute.

Neumann, P. 1997. Salinity resistance and plant growth revisited. Plant, Cell & Environment 20, 1193–1198.

North Dakota Agricultural Weather Network. 2018. Weather data. Available at https://ndawn.ndsu.nodak.edu/. Verified 11 November 2018.

North Dakota Department of Health. 2018. Environmental incident reports. Oilfield environmental incidents. Available online at https://deq.nd.gov/Spills/ . Verified 11 November 2018.

North Dakota Game and Fish Department. 2016. Climate. Available at https://gf.nd.gov/wildlife/habitats/climate. Verified 11 November 2018.

North Dakota State Water Commission. 2016. Facts about North Dakota: Fracking and Water Use. Available online at http://www.swc.nd.gov/pdfs/fracking_water_use.pdf . Verified 11 Nov. 2018.

North Dakota Department of Mineral Resources. 2017. North Dakota annual oil production. North Dakota drilling and production statistics. Available at https://www.dmr.nd.gov/oilgas/ .

North Dakota Department of Mineral Resources. 2013. Oil and Gas Division. Available at https://www.dmr.nd.gov/oilgas/.

Oster, J. D., and I. Shainberg. 2001. Soil responses to sodicity and salinity: challenges and opportunities. Soil Res. 39(6): 1219-1224.

Oster, J. D., I. Shainberg, and I.P. Abrol. 1999. Reclamation of salt-affected soils. Agric. Drain. (38): 659-691.

Oster, J., I. Shainberg and J. Wood. 1980. Flocculation Value and Gel Structure of Sodium/Calcium Montmorillonite and Illite Suspensions. Soil Sci. Soc. Am. J. 44: 955-959.

Oster, J., L. Willardson and G. Hoffman. 1972. Sprinkling and ponding techniques for reclaiming saline soils. Transactions of the ASAE 15: 1115-1117.

Otton, J. K. 2006. Environmental aspects of produced-water salt releases in onshore and coastal petroleum-producing areas of the conterminous US-a bibliography. US Geological Survey Open-File report 2006-1154, p. 223.

Patterson, L.A., Konschnik, K.E., Wiseman, H., Fargione, J., Maloney, K.O., Kiesecker, J., Nicot, J.P., Baruch-Mordo, S., Entrekin, S., Trainor, A., and J.E. Saiers. 2017. Unconventional oil and gas spills: Risks, mitigation priorities, and state reporting requirements. Environ. Sci. Technol. 51: 2563-2573.

Peterman, Z.E., and Thamke, J., 2016, Chemical and isotopic changes in Williston Basin brines during long-term oil production: An example from the Poplar dome, Montana. AAPG Bulletin. 100(10): 1619–1632.

Pettyjohn, W.A. 1971. Water pollution by oil-field brines and related industrial wastes in Ohio. Ohio J. Sci. 71(5): 257-269.

Pitman, J.K., L.C. Price and J.A. LeFever. 2001. Diagenesis and fracture development in the Bakken Formation, Williston Basin: Implications for reservoir quality in the middle member. U.S. Department of the Interior, U.S. Geological Survey.

Prather, R., J. Goertzen, J. Rhoades and H. Frenkel. 1978. Efficient Amendment Use in Sodic Soil Reclamation. Soil Sci. Soc. Am. J. 42: 782-786.

Preston, T. M., and K. Kim. 2016. Land cover changes associated with recent energy development in the Williston Basin; Northern Great Plains, USA. Sci, Tot. Environ. 566: 1511-1518.

Price, L. 1999. Origins and characteristics of the basin-centered continuous-reservoir unconventional oil resource base of the Bakken source system, Williston Basin. EERC, University of North Dakota, Grand Forks, North Dakota.

Pujol, J.A., J.F. Calvo and L. Ramirez-Diaz. 2000. Recovery of germination from different osmotic conditions by four halophytes from southeastern Spain. Ann. Bot. 85: 279-286.

Qadir, M., E. Quillérou, V. Nangia, G. Murtaza, M. Singh, R.J. Thomas, P. Dreschel, and A.D. Noble. 2014. Economics of salt-induced land degradation and restoration. Nat. Resour. Forum 38(4): 282-295.

Qadir, M., J. Oster, S. Schubert, A. Noble and K. Sahrawat. 2007. Phytoremediation of sodic and saline-sodic soils. Adv. Agron. 96: 197-247.

Qadir, M., Steffens, D., F. Yan and S. Schubert. 2003. Sodium removal from a calcareous saline–sodic soil through leaching and plant uptake during phytoremediation. Land Degrad. Dev. 14: 301-307.

Qadir, M., A. Ghafoor and G. Murtaza. 2001. Use of saline–sodic waters through phytoremediation of calcareous saline–sodic soils. Agric. Water Manage. 50: 197-210.

Qadir, M., A. Ghafoor and G. Murtaza. 2000. Amelioration strategies for saline soils: a review. Land Degrad. Dev. 11: 501-521.

Quirk, J. and R. Schofield. 1955. The effect of electrolyte concentration on soil permeability. J. Soil Sci. 6: 163-178.

Reiten, J., Tischmak, T. 1993. Appraisal of oil-field brine contamination in shallow ground water and surface water, eastern Sheridan County, Montana. Montana Bureau of Mines and Geology open file report 260: 296.

Rhykerd, R.L., R.W. Weaver and K.J. McInnes. 1995. Influence of salinity on bioremediation of oil in soil. Environ. Pollut. 90: 127-130.

Ries, R. and L. Hofmann. 1983. Effect of sodium and magnesium sulfate on forage seed germination. J. Range Manage. 36(5): 658-662.

Robbins, C. 1986. Sodic Calcareous Soil Reclamation as Affected by Different Amendments and Crops. Agron. J. 78: 916-920.

Rodriguez, R.S. and D.J. Soeder. 2015. Evolving water management practices in shale oil & gas development. J. Unconv. Oil Gas Resour. 10: 18-24.

Rostron, B.J., L.I. Kelley, L.K Kreis, and C. Holmden. 2002. Economic potential of formation brines: interim results from the Saskatchewan brine sampling program: Saskatchewan Geological Survey. Summary of Investigations v. 2: Saskatchewan Industry Resources Miscellaneous Report 2002- 4.2, CD-ROM, Paper C-1, 29 p.

Sanchez, D.P. 2017. Evaluation of Oil Field Soil Brine Remediation Products. Ph. D. diss. West Texas A&M University.

Schaetzl, R. and S. Anderson. 2005. Soils: Genesis and Geomorphology. Cambridge University Press.

Schmer, M., Q. Xue and J. Hendrickson. 2012. Salinity effects on perennial, warm-season (C4) grass germination adapted to the northern Great Plains. Can. J. Plant Sci. 92: 873-881.

Shainberg, I., D. Warrington and P. Rengasamy. 1990. Water quality and PAM interactions in reducing surface sealing. Soil Sci. 149: 301-307.

Shainberg, I., & Letey, J. 1984. Response of soils to sodic and saline conditions. Hilgardia 52(2): 1-57.

Shaygan, M., T. Baumgartl and S. Arnold. 2017. Germination of Atriplex halimus seeds under salinity and water stress. Ecol. Eng. 102: 636-640.

Shouakar-Stash, O. 2008. Evaluation of Stable Chlorine and Bromine Isotopes in Sedimentary Formation Fluids. M.S. thesis. Louisiana State University and Agricultural and Mechanical College. Available at http://digitalcommons.lsu.edu/gradschool_theses/260 .Verified 6 Apr. 2019.

Smith, C., J. Oster and G. Sposito. 2015. Potassium and magnesium in irrigation water quality assessment. Agric. Water Manage. 157: 59-64.

Sparks, D. L. (Ed.). 1998. Soil physical chemistry. CRC press LLC.

Sposito, G. (1989). The chemistry of soils. Oxford university press, Inc. 134-137.

Steppuhn, H., K. Wall and P. Jefferson. 2009. Seed size effects on emergence, height growth, and shoot biomass of first-year alfalfa grown in saline media. Transactions of the ASABE 52: 121-132.

Suarez D.L., J.D. Wood, and S.M. Lesch. 2008. Infiltration into cropped soils: effect of rain and sodium adsorption ratio – impacted irrigation water. J. Environ. Qual. 37: S169–S179.

Sublette, K.L., J.B. Tapp, J.B. Fisher, E. Jennings, K. Duncan, G. Thoma, J. Brokaw, and T. Todd. 2007. Lessons learned in remediation and restoration in the Oklahoma prairie: A review. Appl. Geochem. 22: 2225-2239.

Swallow, M., & O'Sullivan, G. 2019. Biomimicry of vascular plants as a means of saline soil remediation. Sci. Tot. Environ. 655: 84-91.

Thimm, H. 1990. The prevention of resalinization: the reclamation of saltwater spill sites. J. Can. Petrol. Tech. 29.

Ungar, I.A. 1998. Are biotic factors significant in influencing the distribution of halophytes in saline habitats? Bot. Rev. 64: 176-199.

Ungar, I.A. 1978. Halophyte seed germination. Bot. Rev. 44: 233-264.

United States Department of Agriculture. 2017. State Agriculture Overview: North Dakota. Available online at https://www.nass.usda.gov/Quick_Stats/Ag_Overview/stateOverview.php?state=NORTH%20DAKOTA.Verified 11 Nov. 2018.

United States Energy Information Administration. 2015. North Dakota state energy profile. Available online at https://www.eia.gov/state/print.cfm?sid=ND. Verified 11 Nov. 2018.

United States Environmental Protection Agency. 2018. Basic information about injection wells. Available at http://water.epa.gov/type/groundwater/uic/basicinformation.cfm. Verified 11 Nov. 2018.

Vavrek, M.C, Hunt, H., W. Colgan, and D.L. Vavrek. 2004. Status of oil brine spill site remediation. Proceedings of International Petroleum Environment Conference, October 12-15, Albuquerque, NM, U.S.A.

Veil, J.A., M.G. Puder, D. Elcock and R.J. Redweik Jr. 2004. A white paper describing produced water from production of crude oil, natural gas, and coal bed methane. Argonne National Lab., IL (US).

Vengosh, A., R.B. Jackson, N. Warner, T.H. Darrah and A. Kondash. 2014. A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. Environ. Sci. Tech. 48: 8334-8348.

Wang, N., J.L. Kunz, D. Cleveland, J.A. Stevens and I.M. Cozzarelli. 2019. Biological effects of elevated major ions in surface water contaminated by a produced water from oil production. Arch. Environ. Contam. Toxicol. 1-8.

Whittemore, D.O. 2007. Fate and identification of oil-brine contamination in different hydrogeologic settings. Appl. Geochem. 22: 2099-2114.

Young, M.A., D.G. Rancier, J.L. Roy, S.R. Lunn, S.A. Armstrong and J.V. Headley. 2011. Seeding conditions of the halophyte Atriplex patula for optimal growth on a salt impacted site. Int. J. Phytoremed. 13: 674-680.

Yu, S., Y. Liu, Y. Ai, X. Wang, R. Zhang, Z. Chen, et al. 2018. Rational design of carbonaceous nanofiber/Ni-Al layered double hydroxide nanocomposites for high-efficiency removal of heavy metals from aqueous solutions. Environ. Pollut. 242: 1-11.

Zhang, H., Irving, L. J., Tian, Y., and D. Zhou .2012. Influence of salinity and temperature on seed germination rate and the hydrotime model parameters for the halophyte, Chloris virgata, and the glycophyte, Digitaria sanguinalis. S. Afr. J. Bot. 78: 203-210.

Zhang, K., X.-F. Hua, H.-L. Han, J. Wang, C.-C. Miao, Y.-Y. Xu, Z.-D. Huang, H. Zhang, J.-M. Yang, W.-B. Jin, Y.-M. Liu, and Z. Liu. 2008. Enhanced bioaugmentation of petroleum- and salt-contaminated soil using wheat straw. Chemosphere 73: 1387-1392.

Zhang, X.C., and L.D. Norton. 2002. Effect of exchangeable Mg on saturated hydraulic conductivity, disaggregation and clay dispersion of disturbed soils. J. Hydrol. 260:194-205. doi:10.1016/S0022-1694(01)00612-6

CHAPTER 2: GERMINATION OF SELECTED CROP AND GRAMINOID SPECIES IN RESPONSE TO NACL AND OIL-FIELD BRINE INDUCED SALINITY[1]

Abstract

Oil and gas development is often associated with the production of copious volumes of produced water or “brine”, which is a solution of dissolved salts (NaCl ≈90%) exhibiting electrical conductivities (EC) upwards of 200 dS m^{-1}. Accidental releases of brine to soils inhibits seed germination through osmotic and ionic stressors. The final germination (FG; %) of four crop species: *Hordeum vulgare* (barley), *Helianthus annus* (sunflower), *Carthamus tinctorius* (safflower), *Beta vulgaris* (sugar beet) and four graminoid species: *Pascopyum smithii* (western wheatgrass), *Elymus hoffmannii* (AC Saltlander), *Leymus triticoides* (beardless wildrye), and *Elymus trachycaulus* (slender wheatgrass) were determined using NaCl and brine solutions prepared at EC levels of 0, 4, 8, 16, 24, and 32 dS m^{-1}. No differences ($p >.05$) in FG were found between NaCl and brine solutions across graminoid species or the crop species barley, sunflower, and sugar beet. AC Saltlander had the highest FG (81.9%) at the maximum EC level (32 dS m^{-1}), compared to 47.2% and 0.8% for western wheatgrass and beardless wildrye, respectively. Within crop species, safflower exhibited the highest germination (10-30%) across both solutions at 32 dS m^{-1}. Barley (0-2.9%), sugar beet (4.9-7.7%) and sunflower (0-1.4%) exhibited low germination at 32 dS m^{-1}. The implications of this experiment are that previously established NaCl tolerance indices may be used to accurately determine the FG of

---

[1] The material in this chapter was co-authored by Aaron W. Green, Thomas M. DeSutter, and Miranda A. Meehan. Aaron W. Green had primary responsibility for collecting samples in the field and data analysis. Aaron W. Green was the primary developer of the conclusions that are advanced here. Aaron W. Green also drafted and revised all versions of this chapter. Miranda A. Meehan and Thomas M. DeSutter served as proofreaders and checked the math in the statistical analysis conducted by Aaron W. Green.

plant species in brine-contaminated soils and that AC Saltlander as well as western wheatgrass have the highest FG at 32 dS m^{-1}, indicating these species may have the greatest potential for successfully revegetating brine-contaminated soils.

Introduction

The Williston Basin, which covers portions of North Dakota, Montana, South Dakota, Manitoba, and Saskatchewan, has experienced a significant increase in oil and gas development over the past two decades (Gaswirth et al., 2013). The primary waste product associated with oil and gas extraction consists of produced water or "brine", which is a solution of dissolved salts, drilling chemicals, and emulsified hydrocarbons (Gregory et al., 2011). On average, brines produced near the geographical center of the basin (Williston, ND, USA) exhibit some of the highest levels of total dissolved solids (≥ 250 g L^{-1}) in North America, with the predominant ionic species consisting of Na^+ and Cl^- ($\geq 90\%$) (Clark and Viel, 2009). Although brine disposal has been highly regulated across the region, hundreds of spills of varying sizes have occurred due to pipeline leaks, storage tanks failures, well casing failures and trucking accidents (Gleason et al., 2014). The release of brine to the landscape often results in the mortality of vegetation communities and the saturation of the soil exchange complex with Na (Murphy et al., 1988). Further vegetation growth on these soils often does not occur for months to years following a spill, particularly in semi-arid environments where precipitation is not adequate to effectively leach salts from the soil profile (Keiffer and Ungar, 2002).

Soils contaminated with oil-field brine often exhibit structural and hydraulic characteristics in which only the hardiest plant species can successfully complete their life cycle. High concentrations of Na in the soil profile can cause the deterioration of soil structure by causing clay particles to swell or disperse, reducing the ability of water to infiltrate into and percolate through the soil profile (Zhang and Norton, 2002). In dry seasons, salt migration towards the soil surface results in the formation of hard crusts that restrict infiltration of water and the diffusion of gases into the soil profile (Qadir et al., 2007). In addition, hardsetting of the soil surface may also occur, increasing the bulk density of soil which restricts the proliferation of plant roots (Mullins et al., 1990).

The edaphic properties of soils are also significantly deteriorated by the infiltration of brine into the soil matrix. Although brines consist primarily of Na and Cl, other ionic species that are necessary for seed germination and plant growth including Ca, Mg, and K are also present. The high concentration of these elements, however, render them toxic to vegetation (Keiffer and Ungar, 2002; Munn and Stewart, 1989). Furthermore, the saturation of the soil solution with salts creates an osmotic imbalance between plant roots or seeds and the soil matrix. This osmotic imbalance restricts the absorption of water from the soil, inducing drought-like symptoms to develop in growing plants and seeds to become dormant. (Grieve et al., 2012). High concentrations of salts in the soil solution also restricts adsorption of essential nutrients needed for seed germination and plant growth (Grieve et al., 2012). For example, the absorption of NO_3, K, PO_4, and Ca by plants has been shown to be significantly reduced by the presence of high concentrations of both Na and Cl (Grattan and Grieve, 1999).

In addition to causing nutrient imbalances and osmotic stress in seeds, high levels of salinity often results in ion toxicity through absorption Na and Cl, which restricts germination through the disruption of the metabolic processes required for cell division (Neumann, 1997). In conjunction, the uptake of salts into seeds may result in the expression of oxidative stress in cells, which is caused by an imbalance in the production of various reactive oxygen species (Ibrahim, 2016). High levels of reactive oxygen species in cells often causes cell death by damaging cellular structures such as membrane lipids and enzymes (Ibrahim, 2016; Ashraf and Foolad, 2005).

In-situ or ex-situ remediation of brine-contaminated land is often required in the Williston Basin due to the persistent, deleterious effects of salts on soil health, plant growth, and water quality. The re-establishment of vegetation is often an integral step towards the successful remediation of many brine-contaminated sites. Seed germination is of particular importance in the remediation process, however, little information is available in the literature concerning the germination response of specific plant species to varying levels of salinity caused by oil-field brine (Keiffer and Ungar, 2002; Ungar, 1978). On the other hand, copious amounts of research has been dedicated to the effects of specific salt species on germination (e.g. NaCl).

Germination research that has been conducted in brine-contaminated soils has focused largely on the response of halophytic, or salt-tolerant, plant species for use in phytoremediation, which utilizes plants to hyper-accumulate and/or promote the leaching of salts downwards in the soil profile (Manousaki and Kalogerakis, 2011; Qadir et al., 2007). Many halophytic plant species used in these studies, however, are introduced, scarcely available, costly, or the same species that are controlled as weed species in agricultural settings. These characteristics of halophytic plants often restricts their use by remediation specialists, particularly in the Williston Basin.

The lack of information concerning the germination response of high value or common plant species found throughout the Williston Basin to brine-induced salinity has created a considerable amount of uncertainty for remediation specialists in determining 1) what levels of salinity seeds can tolerate?, 2) what seeding rate is needed to successfully revegetate contaminated sites?, and 3) what species to plant. The purpose of this study was to determine the final germination of four crop and graminoid species across increasing levels of NaCl and oil-field brine induced salinity. The results from this study can then be used to determine any differences in final germination between salt solutions (i.e. NaCl vs. brine), the salinity thresholds at which the selected species can successfully germinate, and the plant species that may be best suited for revegetating brine-contaminated land.

Materials and Methods

The four crop species evaluated were: *Hordeum vulgare* (barley), *Helianthus annus* (sunflower), *Carthamus tinctorius* (safflower), *Beta vulgaris* (sugar beet) and the four graminoid species were: *Pascopyrum smithii* (western wheatgrass), *Elymus hoffmannii* (AC Saltlander), *Leymus triticoides* (beardless wildrye), and *Elymus trachycaulus* (slender wheatgrass). These plant species were chosen based on their availability and relative tolerance to salinity. The tolerance to salinity of the chosen plant species at later stages in their life cycles are provided in Table 2.

Table 2: Salt tolerance indices for crop species (barley, sugar beet, safflower, and sunflower) and graminoid species (beardless wildrye, AC Saltlander, slender, and western wheatgrass).

Plant Species	Production Affected	Plant Mortality	Tolerance Level
	dS m⁻¹	dS m⁻¹	
Beardless Wildrye[†]	13	26	Very High
AC Saltlander[†]	13	26	Very High
Slender Wheatgrass[†]	10	22	Very High
Western Wheatgrass[†]	8	16	High
Barley[†]	8	16	High
Sugar beets[†]	7	13	Moderate
Safflower[†]	6	10	Moderate
Sunflower[‡]	4.8	variable	Moderate

[†] Source: Ogle and St. John (2009).

[‡] Source: Francois (1996).

Seed was obtained from Agassiz Seed & Supply (West Fargo, North Dakota). An equivalent of 20 pure live seeds (PLS) for each crop and graminoid species was calculated, counted, and stored prior to germination testing (Table 3). Sugar beet seed was encapsulated with clay to increase the size of individual seeds for ease of handling. The seed of the other plant species used in this study were not subjected to any form of specialized coating or chemical treatment.

In this study, NaCl and oil-field brine, obtained from a production well in western North Dakota, solutions were prepared at electrical conductivity (EC) levels of 4, 8, 16, 24, and 32 dS m^{-1}, respectively. The EC of the solutions were measured using a Sension 378 conductivity probe (Hach Co., Loveland, CO, USA). Distilled water (0 dS m^{-1}) was utilized as the control in this experiment. NaCl solutions were prepared across EC levels through the addition of various amounts (g) of crystallized NaCl (purity = 99%; VWR International™), to 500 mL of distilled water. Brine solutions were prepared across target EC levels through the addition of various amounts (mL) of brine (EC= 226 dS m^{-1}; SAR= 290) added to 500 mL of distilled water. The cation concentrations (Ca, Mg, Na, and K) across each level of EC for brine and NaCl solutions were determined using an atomic absorption spectrophotometer (Table 4; Model 200A, Buck Scientific).

Table 3: Seed characteristics provided by Agassiz Seed & Supply and germination testing procedures of plant species based on the Association of Official Seed Analysts (AOSA) rules for testing seeds.

Plant Species	Pure Seed (%)	Germination (%)	Pure Live Seed	Substrate	Chill	Temperature (°C)	Photoperiod (h)	Count (d)
AC Saltlander[†]	97.0	90.0	23	T-2[‡]	No	15-25	8:16	7-14-21-28
Beardless wildrye[†]	98.9	95.0	22	P-1[§]	Yes	15-25	8:16	7-14-21-28
Western wheatgrass	96.2	89.0	24	T-1[‡]	No	15-25	8:16	7-14-21-28
Slender wheatgrass	98.0	95.0	22	P-1[§]	Yes	20-30	8:16	14
Sugar beet	49.6	85.0	48	T-1[‡]	No	20-30	8:16	3-7-10
Barley	99.8	90.0	23	T-1[‡]	Yes	20	8:16	7
Safflower	99.5	85.0	24	T-3[‡]	No	20	8:16	4-7-14
Sunflower	99.0	85.0	24	T-3[‡]	No	20	8:16	7

[†] species without AOSA guidelines. Methods for determining the final germination (FG, %) of AC Saltlander and Beardless wildrye were developed by North Dakota State Seed Dept. and are based on professional standards for testing seed.

[‡] T-1, T-2, and T-3 substratum consisted of germination paper of various dimensions that were folded to envelope the tested seed.

[§] P-1 substratum consisted of petri dishes lined with 8.57 cm diameter blotter paper on the bottom with germination placed on top.

Table 4: Cation (K, Na, Mg, Ca) concentrations of NaCl and brine solutions at EC levels of 4, 8, 16, 24, and 32 dS m^{-1}. Distilled water (0 dS m^{-1}) was used as a control.

Solution	EC	K	Na	Mg	Ca
	---dS m^{-1}---	----------mg L^{-1}----------			
Brine	4	29.6	742	12.9	43.0
	8	63.4	1440	28.5	89.1
	16	122	4200	67.2	162
	24	199	5480	92.0	269
	32	279	7900	128	356
NaCl	4	0	840	0	0
	8	0	1800	0	0
	16	0	3540	0	0
	24	0	6020	0	0
	32	0	7560	0	0

Germination testing of both the crop and perennial grass species was conducted at the North Dakota State Seed Lab in Fargo, North Dakota. Methods used for determining the final germination (FG; %) of each of the selected species utilized the Association of Official Seed Analysts (AOSA) rules for testing seed. Three replications of 20 PLS from each species were placed in petri dishes with a base layer of blotter paper and germination paper (beardless wildrye, slender wheatgrass) or wrapped in sheets of germination paper (AC Saltlander, western wheatgrass, sugar beet, barley, sunflower, safflower) that had been thoroughly wetted with either oil-field brine, NaCl, or distilled water solutions prepared at one of the six EC levels. In total, 288 units (8 species*6 EC levels*2 solutions*3 replications) were prepared in this experiment.

Prior to being placed in germination chambers, units containing seed of the species beardless wildrye, slender wheatgrass, and barley were chilled at 4 °C for a period of five, three, and five days, respectively. Chilling, or seed stratification, is necessary to break seed dormancy and allow germination to occur (AOSA, 2010; Bentsink and Koorneef, 2008). The remaining species tested in this study did not require a chill period and thus were placed directly into germination chambers.

Following the initial preparation, units of seed from each species were wrapped in plastic to prevent desiccation and subsequently organized on trays in a completely random design. Seeds were placed in Hoffman Seed Germinators (model no. SG30SC, Hoffman Mfg. Inc. Jefferson, OR, U.S.A.) programmed at temperatures and photoperiod cycles as defined by AOSA standards (Table 3). The germination chambers containing AC Saltlander, beardless wildrye, and western wheatgrass were programmed to alternate between photoperiods of 8 hr of light and 16 hr of dark at temperatures of 15 and 25 °C, respectively. Germination chambers containing barley, safflower, and sunflower seed were programmed to alternate between photoperiods of 8 hr of light and 16 hr of dark at a constant temperature of 20 °C, while chambers containing the sugar beet and slender wheatgrass seed alternated between the same photoperiod at temperatures of 20 to 30 °C, respectively.

Trays were removed from germination chambers following the count days for each species as specified by AOSA guidelines and the seeds from each unit were inspected to identify germinated or abnormal seedlings. Seed from each species was deemed to be successfully germinated when a healthy radicle (first part of the root) and hypocotyl (first leaf) could readily be identified. Successfully germinated seeds were counted, recorded, and disposed of prior to the units being placed back into germination chambers. Abnormal seedlings were identified by a missing or deformed radicle and/or hypocotyl and were either discarded or allowed to remain in the unit until the next counting period to ensure abnormality. Following the final counting period, the number of successfully germinated seeds from each species were tallied by EC level and solution type. The FG was then calculated by dividing the number of successfully germinated seeds by the initial number of seeds tested within each unit (i.e. PLS) and multiplied by 100. To determine whether salt type, EC level, and plant species had a significant effect on the FG of tested seed, a general linear model analysis of variance was used in SAS® (version 9.4, SAS Institute, Inc.) with a Tukey's adjustment and significance determined at the 0.05 level of confidence for crop and graminoid species. The percent contribution to the model was calculated for each of the main and interaction terms of the model for crop and graminoid species to determine how much of the variance could be explained by each term (Table 5).

Results

Crop Species

For crop species, the main effects of species, salt type, and EC level as well as the interactions species*EC level and species*EC level*salt type were significant ($p \leq 0.05$) (Table 5). Overall, EC level (0, 4, 8, 16, 24, and 32 dS m^{-1}) contributed the highest percentage of variation to the model (82.7%), indicating that it had the greatest influence on the FG (%) of the species tested in this study. Species (barley, safflower, sunflower, and sugar beet) and the interaction between species and EC level accounted for 2.61 and 12.4% of variation in the model, respectively, indicating that the particular crop species had a minor impact on the FG of tested seed. Although salt type was found to be significant, it accounted for just 0.43% of the variation in the model. Thus, it may be assumed that it had little overall effect on the FG of tested seed. Similarly, the three-way interaction between species, salt type, and EC level was significant, however, this interaction contributed little to the overall variation present in the model.

Table 5: Analysis of variance for the germination of crop and graminoid species as effected by species, salt type (brine vs NaCl) and electrical conductivity (EC) level with significance determined at an alpha level ≤ 0.05.

SOV	DF	Crop Species			Graminoid Species		
		F Value	Pr > F	% Contribution[†]	F Value	Pr > F	% Contribution[†]
Species[‡]	3	21.2	<.0001	2.61	342	<.0001	44.1
Salt type (brine/NaCl)	1	10.5	0.0017	0.43	3.70	0.0573	0.16
Species*Salt type	3	2.20	0.09	0.27	2.72	0.0485	0.35
EC level (dS m^{-1})[§]	5	403	<.0001	82.7	173	<.0001	37.1
Species*EC level	15	20.2	<.0001	12.4	25.8	<.0001	16.6
EC level*Salt type	5	1.28	0.2780	0.26	0.86	0.5116	0.18
Species*EC level*Salt type	15	2.04	0.0198	1.26	2.24	0.0097	1.44

[†] % Contribution represents the calculated amount of variation in the model that can be explained by each of the main effects or interactions. [% Contribution to the model = (DF * F Value * Mean Squared Error for main effect/interaction)/(Σ DF * F Value * Mean Squared Error for all main effects/interactions)*100].

[‡] Crop Species: *Hordeum vulgare* (barley), *Helianthus annus* (sunflower), *Carthamus tinctorius* (safflower), *Beta vulgaris* (sugar beet).

[‡] Graminoid Species: *Pascopyrum smithii* (western wheatgrass), *Elymus hoffmannii* (AC Saltlander), *Leymus triticoides* (beardless wildrye), Elymus trachycaulus (slender wheatgrass).

[§] EC levels were 0, 4, 8, 16, 24, and 32 dS m^{-1}.

With the NaCl solution, barley, sugar beet, and sunflower exhibited statistically similar FG (98.6-75.0%) at EC levels of 0 and 4 dS m^{-1} (Table 6). Interestingly, safflower had a significantly lower FG (62.5-58.3%) at these levels of EC. At the EC levels of 8 and 16 dS m^{-1}, barley and sugar beet experienced no significant decline in germination to that of the control and maintained significantly higher FG (99.7-84.0%) than that of both sunflower (63.9-54.2%) and safflower (66.7-55.6%). At the highest levels of EC tested using NaCl solutions (24 and 32 dS m^{-1}), significant declines in FG occurred for barley (5.77-2.87%), sugar beet (11.1-7.67%), and sunflower (22.0-0%). In contrast, safflower did not experience a significant decline in FG at an EC level of 24 dS m^{-1} (44.4%) but did, however, have a statistically similar FG to that of the other species tested at 32 dS m^{-1} (11.1%). Using the brine solution, barley (95.7%) and sugar beet (93.1%) had significantly higher FG than both sunflower (69.5%) and safflower (72.2%) at 4 dS m^{-1}. At levels of 8 dS m^{-1}, barley (98.6%) and sunflower (83.3%) had the highest FG of the species tested. At 16 dS m^{-1}, barley (92.8%) and sugar beet (75.7%) again had significantly higher FG than either sunflower (66.7%) and safflower (61.1%) and both species experienced no significant decline in germination from that of the control. At 24 dS m^{-1} (brine), significant declines in FG occurred in barley (27.5%), sugar beet (13.2%), and sunflower (26.4%). Similar to the response observed using NaCl solutions, safflower had significantly higher FG at 24 dS m^{-1} (61.1%). In addition, safflower had a significantly higher FG than that of barley and sunflower at 32 dS m^{-1} (29.1%) when brine was used as the saturating solution.

Table 6: Mean values (with standard deviation) for the germination percentage as affected by electrical conductivity (EC; dS m^{-1}), salt type (NaCl and brine), and crop species. A significant difference found between salt type and FG (%) ($p \leq 0.05$).

Salt Type	EC dS m^{-1}	Barley	Sugar beet	Sunflower	Safflower
NaCl	0	98.6 (2.48) Aa	92.4 (3.15) Aa	90.3 (2.42) Aa	58.3 (4.15) Ba
	4	97.1 (2.48) Aa	75.7 (15.8) Aa	75.0 (4.20) Aab	62.5 (4.20) Ba
	8	99.7 (0.0) Aa	84.0 (9.42) Aa	63.9 (8.65) Bb	66.7 (12.5) Ba
	16	91.3 (4.35) Aa	84.0 (2.36) Aa	54.2 (15.0) Bb	55.6 (2.37) Ba
	24	5.77 (6.62) Bb	11.1 (9.87) Bb	22.2 (12.7) Ac	44.4 (10.5) Aa
	32	2.87 (2.48) Ab	7.67 (9.87) Ab	0.0 (0.0) Ac	11.1 (10.5) Ab
Brine	0	98.6 (2.48) Aa	92.4 (3.15) Aa	90.3 (2.42) Aa	58.3 (4.15) Ba
	4	95.7 (7.51) Aa	93.1 (3.16) ABa	69.5 (8.69) Ca	72.2 (2.42) BCa
	8	98.6 (2.48) Aa	72.2 (9.81) Bb	83.3 (11.0) Aba	70.8 (15.0) Ba
	16	92.8 (6.62) Aa	75.7 (11.8) ABab	66.7 (12.5) BCa	61.1 (12.0) Ca
	24	27.5 (15.3) Bb	13.2 (6.69) Bc	26.4 (10.5) Bb	61.1 (2.42) Aa
	32	0.0 (0.0) Bc	4.87 (4.33) ABc	1.40 (2.42) Bc	29.1 (7.22) Ab

*Upper case letters separate germination (%) means across plant species by EC level and lower case levels separate germination means across EC levels for each individual plant species.

Graminoid Species

In graminoid species, the main effects of species and EC level as well as the interactions of species*salt type, species*EC level and species*EC level*salt type were all found to be statistically significant (Table 5). Species (44.1%), EC level (37.1%), and the interaction between species and EC level (16.6%) contributed to nearly all of variation exhibited by the model and thus had the greatest influence on FG. Although salt type (brine/NaCl) had no significant influence on FG, the two-way interaction between salt type and species as well as the three-way interaction between salt type, species, and EC level were also found to be significant. These interactions, however, contributed little to the overall variation (1.79%) that can be explained by the model.

In Table 7, means and standard deviations for the combination of FG from both brine and NaCl solutions are shown for the four graminoid species across each level of EC tested in this study. Values for FG were combined across salt types for each species and EC level (replications= 6) due to the finding of no significant difference in FG between NaCl and brine solutions. At EC levels of 0, 4, and 8 dS m^{-1}, the FG for AC Saltlander (98.6-92.8%), western wheatgrass (93.1-88.9%), and slender wheatgrass (87.9-83.3%) were all significantly higher than that of beardless wildrye (77.3-32.6%) and, in addition, exhibited no significant decline from that of the control. At 16 dS m^{-1}, a significant decline in FG occurred in slender wheatgrass (45.5%), while AC Saltlander (92.1%) and western wheatgrass (84.1%) experienced no significant decline in FG from that of the control. At an EC of 24 dS m^{-1}, AC Saltlander (84.8%) and western wheatgrass (69.4%) experienced significant declines in FG from the control, however, both were significantly higher than that of beardless wildrye (3.02%) and slender wheatgrass (0.0%). Beardless wildrye (0.75%) exhibited little germination at 32 dS m^{-1}, while western wheatgrass experienced a significant decrease in FG (47.2%) from 24 to 32 dS m^{-1}. Overall, the FG for AC Saltlander at 32 dS m^{-1} (81.9%) was significantly higher than the other graminoid species tested in this study and can be expected to perform the best in salt-impacted environments.

Table 7: Mean values (with standard deviation) for the germination percentage as affected by Electrical Conductivity (EC; dS m^{-1}) and graminoid species. There was no significant difference found between salt type and germination percentage (*$p \leq 0.05$*).

Salt Type	EC dS m^{-1}	AC Saltlander	Western Wheatgrass	Slender Wheatgrass	Beardless Wildrye
NaCl & Brine	0	98.6 (2.22) Aa	93.1 (2.12) ABa	87.9 (2.32) ABCa	77.3 (0.0) BCa
	4	89.9 (6.54) Aabc	88.9 (10.4) Aa	82.6 (12.7) Aa	62.1 (17.9) Ba
	8	92.8 (7.61) Aab	91.0 (7.18) Aa	83.3 (11.0) Aa	32.6 (6.70) Bb
	16	92.1 (5.07) Aabc	84.1 (10.7) Aab	45.5 (21.7) Bb	17.4 (17.6) Cbc
	24	84.8 (7.17) Abc	69.4 (9.74) Ab	0.0 (0.0) Bc	3.02 (3.71) Bc
	32	81.9 (6.40) Ac	47.2 (10.1) Bc	0.0 (0.0) Cc	0.75 (1.84) Cc

*Upper case letters separate germination (%) means across plant species by EC level and lower case levels separate germination means across EC levels for each individual plant species.

Discussion

Salt Type and Germination Response

The germination and growth of various plant species in the presence of soil salinity has been shown in the literature to be dependent not only the concentration of salts in solution (i.e. EC), but also the salt speciation (Grieve et al., 2012). For example, Matthees et al. (2018) found that the germination of pennycress (*Thlaspi arvense L.*) was significantly lower in the presence of Na-based salts than in solutions of Ca-based salts. In another study, Curtin et al. (1993) observed that the growth of barley was significantly better in systems dominated by SO_4-based salts than those containing Cl-based salts. Although predominantly composed of NaCl, the oil-field brine used in this study consisted of various amounts of Ca, Mg, and K, all of which are essential nutrients for plant growth. It is evident, however, that the presence of these essential nutrients had little positive effect on the germination response of the tested graminoid species as well as the crop species consisting of barley, sugarbeet, and sunflower across all levels of salinity. This may be explained by the inhibitory effects of Na which restricts seeds from absorbing these nutrients from solution, causing the seed to exhibit similar FG across both NaCl and brine-based salts. This indicates that previously established values for the FG of these species in NaCl-dominated soils can be extrapolated accurately for use in brine-contaminated soils. In contrast to the other species tested, safflower exhibited a significantly higher FG in the presence of brine-based salt solutions than that observed with NaCl-based salt solutions. Although not readily apparent for the other species tested, it is possible that the presence of Ca, Mg, and K concentration in the brine solutions were sufficient to alleviate the inhibitory effects of Na on safflower seed germination (Kopittke, 2012). There is not sufficient evidence present in this study, however, to definitively make the conclusion that the effects of these cationic species promoted the FG of safflower seed.

Germination Response for Plant Species Among EC Levels

Of the main effects used in the model for crops, EC level contributed the greatest amount of variation (82.7%) and therefore had the greatest impact on FG of tested seeds. This can likely be explained by the abrupt declines in FG for barley, sugar beet, and sunflower at salinities of 24 dS m^{-1} in both NaCl and brine solutions. Similar reductions in germination were found with increasing EC levels of NaCl solutions for barley (Askari et al., 2016; Zhang et al., 2010), sugar beet (Khayamim et al., 2014; Jamil et al., 2006), sunflower (Achakzai, 2014; Bajehbaj, 2010; Liu et al., 2010), and safflower (Siddiqi et al., 2007, Kaya et al., 2003) in the literature and confirm the significant influence of EC level on the FG of these crop species. In contrast, a significant amount of variation in the model for the FG of graminoid species was attributed to the species type (44.1%), which was likely caused by the high and low performance of AC Saltlander and beardless wildrye, respectively, regardless of EC level. Of the species tested in this study, AC Saltlander was the sole species bred specifically to grow in highly saline environments

(Steppuhn et al., 2006). In greenhouse trials testing the emergence, height, and yield of AC Saltlander (e.g. green wheatgrass) in NaCl-$CaCl_2$ solutions prepared at EC levels ranging from 1.5 to 48 dS m^{-1}, Steppuhn and Asay (2005) observed that the emergence and survival of AC Saltlander did not significantly decline until the EC of the solutions reached or exceeded 24 dS m^{-1}. Their findings match well with this study and confirm the high performance of AC Saltlander at high salinities. In contrast, the low performance of beardless wildrye in this study are similar to the findings of Salo et al. (1996), who classified the species as being somewhat salt-tolerant with 50% germination occurring at salinities as low as 1.6 dS m^{-1}.

Management Implications

The germination response of crop and graminoid species to increasing levels of salinity were analyzed separately to reflect differences in life cycles (annual vs. perennial) and land use (cropland vs. pastureland). In cropland situations, where the goals of producers and remediation specialists is not only to provide cover to reduce erosion but also to obtain sufficient return on investment, the results of this study indicate that the germination of barley and sugar beet are not significantly affected at EC levels up to 16 dS m^{-1}. These species would give stakeholders the highest chance of meeting the before stated goals in brine-contaminated soils. In the case of sugar beet, however, its use in brine-contaminated-soils above 4 dS m^{-1} may be limited by the high initial cost of seed (~11 USD kg^{-1}) and the potential for subsequent reseeding should it be needed. Barley seed (0.62 - 2.51 USD kg^{-1}), on the other hand, is relatively inexpensive and thus may provide the lowest amount of financial risk for remediation specialists and producers, alike. In pastureland situations where the goals of remediation are to provide ground cover while also providing palatable forage for livestock, the results of this study indicate that both western wheatgrass and AC Saltlander, both of which are reported in the literature to be palatable for livestock, would provide the highest chance of germination and remediation success in soils exhibiting EC levels up to or exceeding 16 dS m^{-1}, respectively. Although the most successful species of those tested in this study, it is also important to note the high costs associated with both AC Saltlander (~19.30 USD kg^{-1}) and western wheatgrass (~13.11 USD kg^{-1}) seed. In addition, the availability of AC Saltlander may be limited by the small number of vendors who keep seed on hand.

Conclusions

The development of oil and gas resources throughout the Williston Basin, which spans portions of both the U.S. and Canada, has resulted in an ever increasing number of brine spills. Due to the severe salinization of the soil caused by these spills, it is often necessary to implement various remediation strategies to restore land use, which often entails the reestablishment of beneficial vegetation. In this study, seven out of the eight species tested exhibited similar germination responses to various levels of NaCl and oil-field brine induced salinity, indicating previously established germination thresholds using NaCl can be accurately used to inform the selection of salt tolerant plants for revegetation efforts in brine-contaminated lands. Of the crop species tested, barley and sugar beet exhibited high germination rates up to 16 dS m^{-1}, giving these species a higher chance for success in revegetation efforts of brine-contaminated cropland. In graminoid species, AC Saltlander exhibited little decline in FG up to the maximum EC level of 32 dS m^{-1}, potentially making it the most effective species in brine-contaminated pasturelands.

References

Achakzai, A. K. K. 2014. Imbibition, germination and lipid mobilization response by sunflower subjected to salt stress. Pak. J. Bot. 46(6): 1995-2002.

AOSA. 2010. Rules for Testing Seeds: Seedling Evaluation. AOSA, ed. AOSA, Washington, DC.

Ashraf, M. and M.R. Foolad. 2005. Pre-sowing seed treatment-a shotgun approach to improve germination, plant growth, and crop yield under saline and non-saline conditions. Adv. Agron. 88, 223–271. Doi: 10.1016/S0065-2113(05)88006-X.

Askari, H., Kazemitabar, S. K., Zarrini, H. N., and M. H. Saberi. 2016. Salt tolerance assessment of barley (Hordeum vulgare L.) genotypes at germination stage by tolerance indices. Open Agric. J. 1(1).

Bajehbaj, A. A. (2010). The effects of NaCl priming on salt tolerance in sunflower germination and seedling grown under salinity conditions. Afr. J. Biotechnol. 9(12).

Bentsink, L., and M. Koornneef. 2008. Seed dormancy and germination. The Arabidopsis Book/American Society of Plant Biologists, 6.

Clark, C. and J. Veil. 2009. Produced water volumes and management practices in the United States. Argonne National Lab, Argonne, IL, United States.

Curtin, D., Steppuhn, H., and F. Selles. 1993. Plant responses to sulfate and chloride salinity: growth and ionic relations. Soil Sci. Soc. Amer. J. 57(5): 1304-1310.

Francois, L. E. 1996. Salinity effects on four sunflower hybrids. Agron. J.,88 (2): 215-219.

Gaswirth, S.B., K.R. Marra, T.A. Cook, R.R. Charpentier, D.L. Gautier, D.K. Higley, T.R. Klett, M.D. Lewan, P.G. Lillis, C.J. Schenk, M.E. Tennyson, and K.J. Whidden. 2013. Assessment of undiscovered oil resources in the bakken and three forks formations, Williston Basin Province, Montana, North Dakota, and South Dakota, 2013. U.S. Geological Survey Fact Sheet 3013.

Gleason, R.A., T.L.C. Chesley-Preston, J.L. Coleman Jr., S.S. Haines, K.E. Jenni, T.L. Nieman, Z.E. Peterman, M.P. van der Burg, T.M. Preston, B.D. Smith, B.A. Tangen, and J.N. Thamke. 2014. Brine contamination to aquatic resources from oil and gas development in the Williston Basin, United States. No. 2014-5017. U.S. Geological Survey. doi:10.3133/sir20145017.

Grattan, S. and C. Grieve. 1998. Salinity–mineral nutrient relations in horticultural crops. Sci. Hortic. 78: 127-157.

Gregory, K.B., R.D. Vidic and D.A. Dzombak. 2011. Water management challenges associated with the production of shale gas by hydraulic fracturing. Elem. 7: 181-186.

Grieve, C.M., S.R. Grattan and E.V. Maas. 2012. Plant salt tolerance. Agric. Salinity Assess. and Manage. 2: 405-459.

Ibrahim, E. A. 2016. Seed priming to alleviate salinity stress in germinating seeds. J. Plant Physiol. 192: 38-46.

Jamil, M., Deog Bae, L., Kwang Yong, J., Ashraf, M., Sheong Chun, L., and R. Eui Shik. 2006. Effect of salt (NaCl) stress on germination and early seedling growth of four vegetables species. J. Cent. Eur. Agric. 7(2): 273-282.

Kaya, M. D., Ipek, A., and A. Öztürk. 2003. Effects of different soil salinity levels on germination and seedling growth of safflower (Carthamus tinctorius L.). Turk. J. Agric. For. 27(4): 221-227.

Keiffer, C.H. and I.A. Ungar. 2002. Germination and establishment of halophytes on brine-affected soils. J. Appl. Ecol. 39: 402-415.

Khayamim, S., Rouzbeh, F., Poustini, K., Sadeghian, S. Y., Abbasi, Z., and R.T. Afshari. 2018. Seed germination, plant establishment, and yield of sugar beet genotypes under salinity stress. J. Agric. Sci. Technol. 16: 779-790.

Kopittke, P. M. 2012. Interactions between Ca, Mg, Na and K: alleviation of toxicity in saline solutions. Plant and Soil. 352(1-2): 353-362.

Liu, J., Guo, W. Q., and D.C. Shi. 2010. Seed germination, seedling survival, and physiological response of sunflowers under saline and alkaline conditions. Photosynthetica. 48(2): 278-286.

Manousaki, E. and N. Kalogerakis. 2011. Halophytes—an emerging trend in phytoremediation. Int. J. Phytorem. 13: 959-969.

Matthees, H. L., Thom, M. D., Gesch, R. W., and F. Forcella .2018. Salinity tolerance of germinating alternative oilseeds. Ind. Crops Prod. 113: 358-367.

Mullins, C. E., MacLeod, D. A., Northcote, K. H., Tisdall, J. M., and I.M. Young. 1990. Hardsetting soils: behavior, occurrence, and management. Adv. Soil Sci. 11: 37-108.

Munn, D.A. and R. Stewart. 1989. Effect of oil well brine on germination and seedling growth of several crops. Ohio J. Sci. 89(4): 92-94.

Murphy, E.C., A.E. Kehew, G.H. Groenewold and W.A. Beal. 1988. Leachate generated by an oil-and-gas brine pond site in North Dakota. Groundwater 26: 31-38.

Neumann, P. 1997. Salinity resistance and plant growth revisited. Plant, Cell & Environment 20: 1193–1198.

Ogle, D. and L. St. John. 2010. Plants for saline to sodic soil conditions. Technical note No. 43. United States Department of Agriculture-Natural Resources Conservation Service.

Salo, L. F., Artiola, J. F., and J.W. Goodrich-Mahoney. 1996. Plant species for revegetation of a saline flue gas desulfurization sludge pond. J. Environ. Qual. 25(4): 802-808.

SAS Institute Inc. 2013. SAS® 9.4 [Computer software]. Cary, NC, USA.

Siddiqi, E. H., Ashraf, M., and N.A. Akram. 2007. Variation in seed germination and seedling growth in some diverse lines of safflower (Carthamus tinctorius L.) under salt stress. Pak. J. Bot. 39(6): 1937-1944.

Steppuhn, H., Jefferson, P. G., Iwaasa, A. D., and J.G. McLeod. 2006. AC Saltlander green wheatgrass. Can. J. Plant Sci. 86(4): 1161-1164.

Steppuhn, H. and K. Asay. 2005. Emergence, height, and yield of tall, NewHy, and green wheatgrass forage crops grown in saline root zones. Can. J. Plant Sci. 85(4): 863-875.

Ungar, I.A. 1978. Halophyte seed germination. Bot. Rev. 44: 233-264.

Qadir, M., J. Oster, S. Schubert, A. Noble and K. Sahrawat. 2007. Phytoremediation of sodic and saline-sodic soils. Adv. Agron. 96: 197-247.

Zhang, H., Irving, L. J., McGill, C., Matthew, C., Zhou, D., and P. Kemp. 2010. The effects of salinity and osmotic stress on barley germination rate: sodium as an osmotic regulator. Annals of Botany. 106(6): 1027-1035.

Zhang, X.C., and L.D. Norton. 2002. Effect of exchangeable Mg on saturated hydraulic conductivity, disaggregation and clay dispersion of disturbed soils. J. Hydrol. 260:194-205. doi:10.1016/S0022-1694(01)00612-6

CHAPTER 3: WICKING SALTS FROM BRINE-CONTAMINATED SOILS: POTENTIAL METHOD FOR IN-SITU REMEDIATION[2]

Abstract

Accidental releases of brine, derived from oil and gas development, in the Williston Basin have become frequent in recent years. Oil-field brines are primarily composed of sodium chloride and exhibit electrical conductivities (EC) and total dissolved solids (TDS) exceeding 200 dS m^{-1} and 250 g L^{-1}, respectively. Current in-situ remediation strategies involve the incorporation of divalent-cation rich amendments to displace and then rain/irrigation to leach sodium out of the soil profile. These methods in semi-arid climates, where the evaporative demand exceeds precipitation, often achieves limited results. This study assessed the feasibility of remediating brine-contamination by "wicking" salts from the soil surface when a shallow water table is present. During a five week period, two engineered paper-based humidifier wicks and two non-engineered wicks (wheat straw and hydraulic mulch) placed on the surface of brine-contaminated soils reduced the total soil Na concentrations by 65-88% and 5-80%, respectively. Based on this study, deployment of engineered wicks may be a feasible in-situ remediation strategy for brine-contaminated soils.

---

[2] Chapter 3 has been published in *Agricultural and Environmental Letters* with the citation:

Green, A.W., T.M. DeSutter, A.L. Daigh and M.A. Meehan. 2019. Wicking Salts from Brine-Contaminated Soils: A Potential Method for In Situ Remediation. Agric. Environ. Lett. 4(1). doi:10.2134/ael2018.12.0069

Aaron W. Green was the lead author on the publication and had the primary responsibility for all data collection, analysis, interpretation, and manuscript preparation.

Introduction

The production of oil and gas from the Bakken and Three Forks formations in Western North Dakota has increased exponentially over the past decade. During oil extraction, upwards of 18 barrels of salt water or "brine" are produced for each barrel of oil (Clark and Viel, 2009). Accidental releases of brine have become a common occurrence over the past decade. Brines produced in the region are largely composed of NaCl and exhibit electrical conductivities (EC) of 200 dS m^{-1} (Gleason, 2014; Lauer, 2016). In the event of a release, the chemistry of brine often causes the disturbance of soil structure and vegetation mortality.

Brine spill mitigation utilizing the ex-situ method of excavation and removal (i.e. dig and haul) is the predominant practice used in Williston Basin. Dig and haul provides an expedient and effective method of contaminant removal, however the financial costs (2,650 USD m^{-3}; D. Anderson, personal communication, 2018) and the scarcity of suitable replacement soil diminishes its applicability in some situations. In-situ remediation of brine-contaminated soils is often attempted through the provision of divalent cations to displace Na from soil exchange sites and subsequent leaching by precipitation events or irrigation to remove it from the topsoil. In semi-arid climates such as Williston Basin, where annual evaporative demand is often four times that of annual precipitation, the potential for resalinization of the topsoil through upward capillary rise causes this method to be time-intensive and costly while often achieving limited results (Harris et al., 2005). Given the limitations of traditional methods, novel forms of in-situ remediation from the soil surface through the use of crystallization inhibitors and the capillary rise of water and dissolved salts have been presented in the literature with promising results (Swallow and O'Sullivan, 2019; Daigh et al. 2017). The objective of this proof-of-concept study was to determine the efficacy of using highly absorbent "wicking" materials to draw water and dissolved salts from the soil profile, without the use of a crystallization inhibitor, as a means of permanent salt removal (Figure 2A). We hypothesize that under constant soil water conditions and the presence of a high evaporative demand, significant quantities of sodium may be removed from brine-contaminated soils.

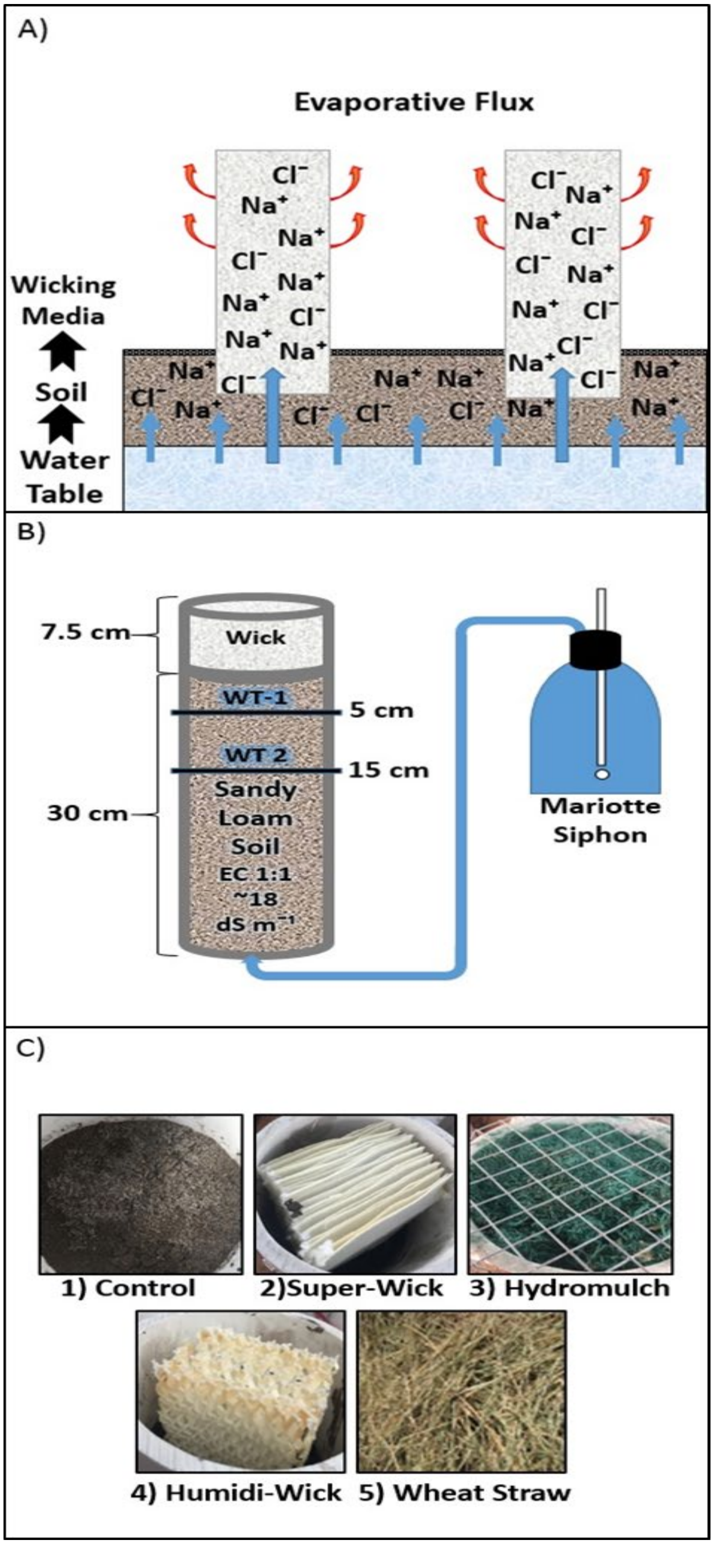

Figure 2: Diagram showing (A) Conceptual illustration of proposed method, (B) Schematic for soil column set-up and water table depths (i.e. WT-1, WT-2), and (C) Illustration of wicking treatments used in the experiment.

Materials and Methods

This study was conducted over a five week period (Nov. 13th-Dec. 18th, 2017) in a greenhouse located on the campus of North Dakota State University (Fargo, North Dakota). Mean air temperature and relative humidity within the greenhouse were 26.5 ± 3.2°C and 18.6 ± 0.07%, respectively.

To simulate brine-contamination, 3.3 kg batches of a fine sandy loam soil ($EC_{1:1} < 0.5$ dS m^{-1}) were mechanically mixed with 265 mL of oil field brine (EC ≈ 226 dS m^{-1}). After mixing, the soil was allowed to air dry for a 7-d period before being ground to pass a 2-mm sieve and mixed again for a five minute period. The resulting brine and soil mixtures exhibited average $EC_{1:1}$ and %Na values of 18 dS m^{-1} and 70.5, respectively. The soil was then packed into 30 polyvinyl chloride (PVC) columns (10.2 cm diameter by 38.1 cm height) to 30 cm depths (Figure 2B). The top of each column was left open to the atmosphere to allow for the placement of wicking materials and permit an evaporative flux. The bottom of each column was sealed using a PVC test cap modified with a nylon garden hose barb. Water reservoirs consisted of 30 four-L Mariotte siphons filled with degassed, purified water (reverse osmosis), and sealed using #6 rubber stoppers containing two separate 0.16 cm by 0.32 cm tubes to act as a water supply line and air intake, respectively. Siphons were connected to each soil column and assigned one of two water table depths at 5 cm (WT-1) and 15 cm (WT-2) below the soil surface (Figure 2B). Wicking treatments were (I) a bare soil surface [(control (C)] (II) ground wheat straw (S), (III) Second Nature® Wood Fiber Plus Hydraulic Mulch (Profile Products®) (HM), (IV) 1043 Super Wick (Essick Air Products, Inc.) (SW), and (V) CBW9 Humidi-Wick (BestAir Pro®) (HW) (Figure 2C). Soil columns were then placed into wooden stands in a completely random arrangement.

The S and HM were placed into soil columns to form 7.5 cm thick layer above the soil surface. The SW and HW materials were placed into the soil to a depth 2.5 cm (7.5 cm areal height). Wicking materials were carefully removed and any soil adhering to the wicks were placed back into the column and replaced at 7-d intervals. Evaporation losses (mL d^{-1}) were determined by recording the weight (g) of the Mariotte siphons daily over 14-d. Following the cessation of the experiment, soil columns were frozen at temperatures of -12° C for 3-d. Once frozen, columns were cut and the soil was dissected into 5 cm sections. Soil samples were air-dried, weighed, and prepared using 1:20 soil/1M ammonium acetate (pH = 7). Cation concentrations (Na, Mg, and Ca) from the extracts were determined using an atomic absorption spectrophotometer (Model 200A, Buck Scientific). $EC_{1:1}$ of soil samples were measured from suspensions of 10 g soil and 10 mL of deionized water using a Sension 378 conductivity probe (Hach Co., Loveland, CO, USA). Wicking materials were washed in one L of distilled water and the extracts quantified for Na, Mg, and Ca and EC as above. A mass balance analysis was then conducted to determine the total mass Na^+ reduction (%) from each of the soil columns by:

$\%Na\ reduction = 100wick_f/(wick_f + soil_f)$ [2]

Where $wick_f$ is the Na^+ extracted by the wicking material and $soil_f$ is the Na remaining in the soil expressed on a mass basis (mg).

To determine if water table depth and wicking material affected the % reduction of Na in the soil profile and the average rate of evaporation, a mixed model analysis of variance was used in SAS with a Tukey's adjustment at the 0.05 level of confidence (version 9.4, SAS Institute, Inc.). No reduction in Na occurred in columns with no wicking material (i.e. control) and thus were not compared to the other treatments. Regression analysis was used to determine the relationship between average evaporation rate (mL d^{-1}) and total mass Na reduction in the soil (%) and fit by a logarithmic model in SigmaPlot 10.0 (2006 Systat Software, Inc. San Jose, CA).

Results and Discussion

Over a five week period, the wicking treatments: SW, HW, HM, and S reduced the mass of Na in the soil columns by an average of 87, 74, 79, 39%, respectively, at WT-1 (Fig. 2A). Similarly, the wicking treatments SW, HW, HM, and S decreased the mass of Na in the soil profile by an average of 88, 81, 60, and 14%, respectively, at WT-2. No significant difference ($p > 0.05$) in percent Na reduction occurred between the two water table depths (WT-1 and WT-2) for SW, HW, and the HM wicking treatments. However, water table depth did significantly affect the reduction of Na in the soil for the S wicking treatment. The ratio of average daily evaporation rate (mL d^{-1}) between the control and each of the respective wicking materials at both water table depths is presented in Figure 3A. The average evaporation rate for the HW at WT-1 (32.9 mL d^{-1}) and for the SW at both WT-1 (32.7 mL d^{-1}) and WT-2 (30.9 mL d^{-1}) were significantly higher than the control (23.6 mL d^{-1}), while the HW at WT-2 (22.6 mL d^{-1}) and the HM at WT-1 (24.8 mL d^{-1}) and WT-2 (23.2 mL d^{-1}) exhibited no significant differences. The relationship between water loss through evaporation into the atmosphere (mL d^{-1}) and reduction of Na (%) was fit using a logarithmic model and was found to be highly significant ($p < .0001$) (Figure 3B).

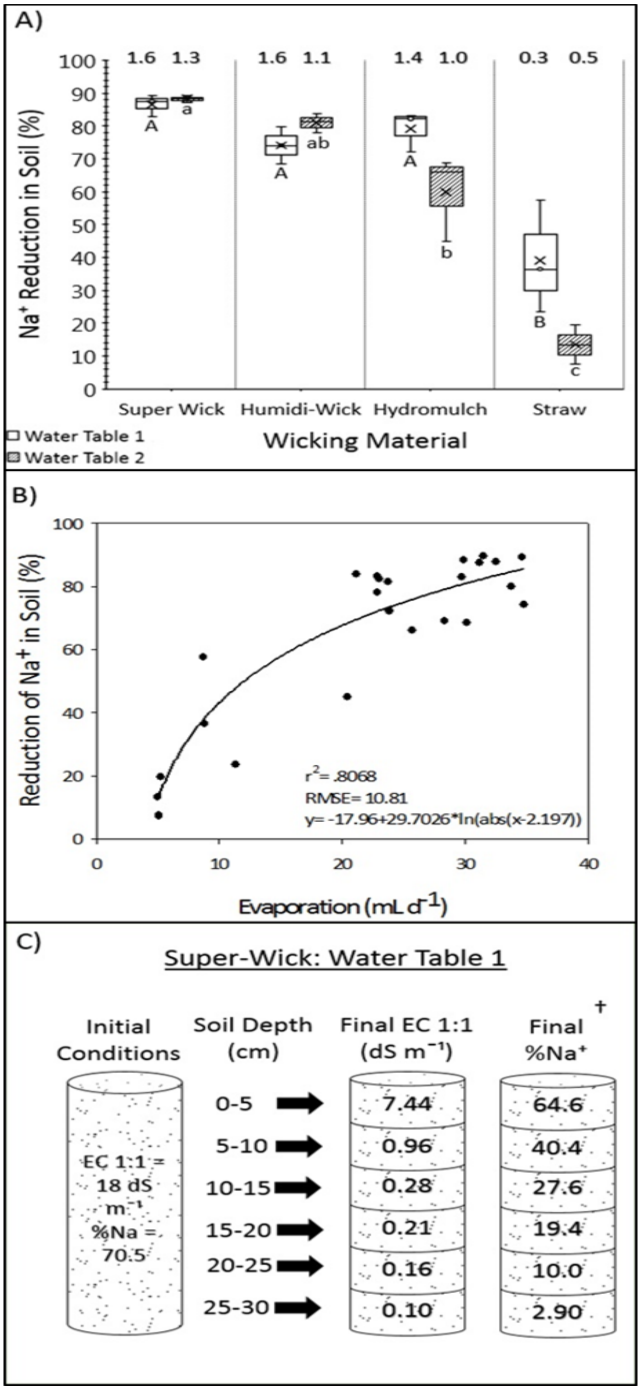

Figure 3: Depiction of (A) Na reduction in the soil (%) by wicking material and water table depth (upper (WT-1) and lower (WT-2) case letters represent significant differences in Na reduction; ratios of evaporation rate between wicking treatment, water table depth, and the control are shown above respective box plots), (B) Relationship between Na reduction (%) and daily evaporation rate (mL d^{-1}), and (C) Initial and Final EC 1:1 and %Na[†] for SW and WT-1 treatments.

[†] %Na calculated using method presented in DeSutter et al. 2015.

The amount of soluble salts accumulated by the wicking materials was dependent on the soil water content, the difference in matric potential between the soil matrix and the material, and the evaporative demand of the atmosphere. Wicking treatments that absorbed greater amounts of water from the soil (i.e. SW, HW, and HM), as indicated by higher daily evaporation rates, were able to accumulate the largest quantities of Na over the 35-d period of the experiment. The capillary suction exerted SW, HW, and HM was greater than that of S due to the distribution of fine-sized pores in these materials. The size distribution of straw used in this experiment (>2.5 cm) most likely did not provide the necessary pore size distribution and pore connectivity to draw water out of the soil profile, thereby reducing the effectiveness of this material to decrease Na concentrations in the soil.

The likelihood of soils exhibiting high concentrations of Na occupying soil exchange sites and in the solution phase to undergo swelling and dispersion is determined by the soil texture, dominant clay mineralogy, and the electrolyte concentration of the soil solution (Quirk, 2001; Zhang and Norton, 2002). Swelling and dispersion can significantly restrict water movement into and through the soil profile. In soils exhibiting elevated levels of exchangeable Na, soil flocculation and water movement can be maintained if the EC of the soil solution is above a critical threshold (Suarez et al., 2008). In this study, as salts were removed from the soil by the wicking materials, the EC of the soil solution decreased at depths between 5 and 30 cm (Fig. 3C). The reduction of soil EC to <1 dS m^{-1}, however, did not cause Na to have significant effect on soil physical properties or water movement, as the soil used in this experiment had a relatively low percentage of clay (<8%). In applications of this method to other soil textures, a source of divalent cations (i.e. Ca) may need to be provided over time to maintain electrolyte concentrations in the soil solution to prevent swelling and dispersion.

Conclusions

In-situ remediation of brine-contaminated soils by the placement of highly absorbent wicking materials onto the soil surface may provide a low disturbance alternative to conventional ex-situ and in-situ remediation methods, particularly in sensitive environments such as wetlands and areas with high water tables. Wicking materials in this study reduced the mass of Na in the soil profile by as much as 88% over a 35-d period. Further research is needed to (I) determine the effectiveness of this method in other soil textures, (II) identify wicking materials that can maximize salt-uptake as well as withstand field conditions, and (III) determine the most effective placement and layout in field conditions to maximize salt reduction.

References

Clark, C. and J. Veil. 2009. Produced water volumes and management practices in the United States. Argonne National Lab., Argonne, IL, United States. doi:10.2172/1007397.

DeSutter, T., D. Franzen, Y. He, A. Wick, J. Lee, B. Deutsch, and D. Clay (2015). Relating sodium percentage to sodium adsorption ratio and its utility in the Northern Great Plains. Soil Sci. Soc. of Am. J. 79(4): 1261-1264.

Gleason, R.A., T.L.C. Chesley-Preston, J.L. Coleman Jr., S.S. Haines, K.E. Jenni, T.L. Nieman, Z.E. Peterman, M.P. van der Burg, T.M. Preston, B.D. Smith, B.A. Tangen, and J.N. Thamke. 2014. Brine contamination to aquatic resources from oil and gas development in the Williston Basin, United States. No. 2014-5017. US Geological Survey. doi:10.3133/sir20145017.

Harris, T.M., J. Bryan Tapp and K.L. Sublette. 2005. Remediation of oil-field brine-impacted soil using a subsurface drainage system and hay. Environ. Geosci. 12: 101-113.

He, Y., T.M. DeSutter, and D.E. Clay. 2013. Dispersion of pure clay minerals as influenced by calcium/magnesium ratios, sodium adsorption ratio, and electrical conductivity. Soil Sci. Soc. of Am. J., 77(6): 2014-2019.

Klaustermeier, A.W., A.L. Daigh, R.F. Limb and K. Sedivec. 2017. Crystallization inhibitors and their remediation potential on brine-contaminated soils. Vadose Zone J. 16(4). doi:10.2136/vzj2016.10.0095.

Quirk, J.P. 2001. The significance of the threshold and turbidity concentrations in relation to sodicity and microstructure. Aust. J. Soil Res. 39: 1185-1217.

Suarez D.L., J.D. Wood, and S.M. Lesch. 2008. Infiltration into cropped soils: effect of rain and sodium adsorption ratio – impacted irrigation water. J Environ. Qual. 37: S169–S179.

Swallow, M., and G. O'Sullivan. 2019. Biomimicry of vascular plants as a means of saline soil remediation. Sci. Total Environ. 655: 84-91.

Zhang, X.C., and L.D. Norton. 2002. Effect of exchangeable Mg on saturated hydraulic conductivity, disaggregation and clay dispersion of disturbed soils. J. Hydrol. 260: 194–205. doi:10.1016/S0022-1694(01)00612-6.

CHAPTER 4: BRINE SPILL REMEDIATION UTILIZING CAPILLARY TRANSPORT AND WICKING MATERIALS: EFFICACY IN LOAM AND SILTY CLAY SOILS[3]

Abstract

During oil and gas extraction within the Bakken and Three Forks shale-oil reserves, highly saline water, or brine, is also extracted. The accidental release of brines into the environment often causes soils to exhibit poor structural and edaphic properties. Due to these effects, active remediation is often attempted through the use of a variety of in-situ and ex-situ techniques, however, many of the conventional methods used are often time intensive, costly, and only partially successful. The purpose of this study was to determine whether salts could be quickly and effectively removed from coarse and fine-textured soils through the surficial applications of an engineered, paper-based humidifier wick or ground wheat straw and irrigated with either purified water or a gypsum solution. Over a period of 56-d, soil columns containing silty clay and loam soils treated with the humidifier wick and sub-irrigated with a saturated gypsum exhibited average reductions of extractable Na of 89.5 and 38.4%, respectively. In columns with the humidifier wick and purified water treatments, reductions of 86.7 and 16.0% were observed between loam and silty clay soils, respectively. The results of this study indicate that the effectiveness of evaporative wicks in removing salts is comparable to other surficial remediation techniques that have previously been tested in laboratory settings.

---

[3] The material in this chapter was co-authored by Aaron W. Green, Thomas M. DeSutter, Aaron L.M. Daigh and Miranda A. Meehan. Aaron W. Green had primary responsibility for collecting samples in the field and analyzing data. Aaron W. Green was the primary developer of the conclusions that are advanced here. Aaron W. Green also drafted and revised all versions of this chapter. Miranda A. Meehan, Aaron L.M. Daigh and Thomas M. DeSutter served as proofreaders and checked the math in the statistical analysis conducted by Aaron W. Green.

Introduction

The increasing demand for energy derived from fossil fuels, in combination with advances in drilling technologies, including hydraulic fracturing and horizontal drilling, has resulted in the rapid development of previously infeasible oil and gas reserves throughout the world (Vengosh et al., 2014). Oil and gas production from these reserves often results in the co-production of significant volumes of produced water or “brine” (Clark and Viel, 2009). Brine derived from oil production is an emulsion of dissolved salts (NaCl), drilling chemicals, and oil (Guerra et al., 2011). The total dissolved solids (TDS) of these brines are often highly variable between producing formations with values ranging from 1 to 450 g L^{-1} (Gleason et al., 2014; Guerra et al., 2011). Although the disposal of these brines has been regulated in many oil and gas producing regions throughout the world, accidental releases frequently occur due to pipeline leaks, storage tank failures, and trucking accidents.

Following a release, brine infiltrates into the soil and the dissolved ions in solution, primarily the monovalent cation Na, can occupy negatively charged clay and organic matter exchange sites through mass action (Hanor, 2007). High levels of exchangeable Na in the soil profile often results in plant mortality, restricted plant growth, and the deterioration of soil structural and hydraulic properties (Keiffer and Ungar, 2002). In the presence of Na or Mg (Rengasamy et al., 1986), the deterioration of soil structure often occurs through the swelling and/or dispersion of clay particles as the electrical conductivity (EC) of the soil solution falls below a particular threshold. This threshold is primarily determined by soil texture, clay mineralogy, and the EC of the soil solution (Marchuk and Rengasamy, 2011; Shainberg and Letey, 1984). In semi-arid and arid environments, where annual precipitation rates are exceeded by the evaporative demand of the atmosphere, salt concentrations often persist at high levels throughout the soil profile due to the upward capillary transport of soil water and dissolved salts towards the soil surface (Thimm, 1990; Murphy et al., 1988). The potential for brine contamination to spread to adjacent land or water resources as well as the long term impacts (i.e. months to years) of salts on soil quality and plant production often necessitates the active remediation of these sites. Conventional in-situ and ex-situ remediation techniques for brine-contaminated land are often costly, time-intensive, and in many instances achieve only partial or short term remediation success (Angin et al., 2018; Young et al., 2011; Harris et al., 2005).

The limitations of current techniques, in conjunction with the rising number of brine spills associated with increased energy exploration throughout the world, has created a pressing need for the development of more cost-effective, expedient, and permanent remediation techniques. For these reasons, contemporary research has investigated the efficacy of harvesting salts via the soil surface (Green et al., 2019; Swallow and O'Sullivan, 2019; Klaustermeier et al., 2017). In concept, surficial remediation may provide a number of advantages when compared with other conventional methods. Conventional methods of remediation often focus on the downward translocation of salts in the soil profile or the complete removal of the native soil through excavation. In comparison, the advantages of surficial remediation techniques may include the permanent removal of salts from soil and groundwater systems, low disturbance to the soil profile, and savings in both time and financial resources (Klaustermeier et al., 2017). One of the more recent surficial remediation techniques was proposed by Klaustermeier and Daigh (2016) utilizing the crystallization inhibitor ferric hexacyanoferrate ($Fe_4 [Fe (CN)_6]_3$) to induce hopper crystal growth of NaCl on the soil surface. In soil column trials conducted over a period of 7-d, the surficial application of the inhibitor resulted in total salt reductions of 46, 57, and 29% in sandy loam, loam, and silty clay soils, respectively (Klaustermeier et al., 2017;

Klaustermeier and Daigh, 2016). Further laboratory research utilizing a wicking medium (Jiffy Strips® peat pots) treated with the crystallization inhibitor potassium cyanoferrate was conducted by Swallow and O'Sullivan (2019). On average, their methodology resulted in total reductions in salt concentrations between 90 and 23% in a clay loam soil (Swallow and O'Sullivan, 2019). Although proven effective in laboratory trials, the use of crystallization inhibitors to remediate contaminated soils in field settings has been met with limited results and further field-scale research has not been conducted. In contrast to surficial methods which utilize a crystallization inhibitor, we hypothesize that the placement of highly absorbent "wicking" materials on the soil surface could be used to accumulate and remove salts from brine contaminated soils through similar capillary mechanisms (Green et al., 2019).

The purpose of this study was to investigate the ability of two materials, an engineered, paper-based humidifier wick and ground wheat (*Triticum aestivum*) straw, to accumulate salts from the surface of silty clay and loam textured soils given that water conditions are maintained near saturation. An additional goal of this research was to determine whether a saturated solution of gypsum would enhance the removal of Na from contaminated soil columns while, in addition, promoting soil flocculation and water movement in comparison to other columns sub-irrigated with distilled (DI) water. Though the specific wicking materials tested in this study may not be applicable in field conditions due to feasibility or practicality, the overall purpose of this study was to provide conceptual evidence to encourage further research towards the economical use of this method in field-scale trials.

Materials and Methods

This study was conducted over an eight week period (Aug. 6th-Oct. 1st, 2018) in a greenhouse located on the campus of North Dakota State University (Fargo, North Dakota).

Mean air temperature and relative humidity within the greenhouse over this period were 20.7 ± 3.2°C and 68.3 ± 12.4%, respectively. Two brine-contaminated soils with loam (427, 432, 140 g kg^{-1} sand, silt, and clay, respectively) and silty clay (117, 430, 453 g kg^{-1} sand, silt, and clay, respectively) textures from the Williston Basin in western North Dakota were air-dried, ground to pass a 2-mm sieve, and analyzed for cation concentrations at AGVISE Laboratories (Northwood, ND). Calcium (Ca^{2+}), Mg^{2+}, Na^{+}, and K^{+} were extracted from the exchanger and solution phases (i.e. extractable) using 1:10 soil/1M ammonium acetate (pH = 7) ratio, filtered, and cations quantified using inductively-coupled plasma spectrometry (Optima 5300V, PerkinElmer, Waltham, MA). To determine the EC of the two soils, samples were prepared using 1:1 suspensions of soil and DI water and measured using a Sension 378 conductivity probe (Hach Co., Loveland, CO, USA). The extractable Na of each soil (i.e. %Na) was calculated using the methodology outlined by DeSutter et al. (2015), which is correlated closely with values of both the sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP). The loam soil had an $EC_{1:1}$ value of 16.3 dS m^{-1} and %Na of 44.9%, while the silty clay soil had an $EC_{1:1}$ value of 13.1 dS m^{-1} and %Na of 26.6%. The silty clay soil also exhibited high initial Ca^{2+} concentrations (8130 ± 418 mg kg^{-1}), indicating that this soil may have previously been amended with a Ca^{2+} amendment such as gypsum ($CaSO_4$). The clay mineralogy of the loam and silty soils were determined by X-ray diffraction with the loam soil consisting predominately of illite (50%) and the silty clay soil primarily consisting of smectitic clays (78%).

Silty clay ($n = 18$; $p_b = 1.14$ g cm^{-3}) and loam soils ($n = 18$; $p_b = 1.22$ g cm^{-3}) were packed into polyvinyl chloride (PVC) columns (10.2 cm diameter by 38.1 cm height) to a depth of 30.5 cm, respectively. The top of each column was left open to the atmosphere to allow for the placement of wicking materials and permit an evaporative flux. The bottom of each column was sealed using a PVC cap modified with a nylon garden hose barb. Each soil column was connected to a 4-L bottle modified to act as a Mariotte siphon which could maintain the soil water conditions in each column near saturation. Each Mariotte siphon was filled with either DI water (n = 18) or a gypsum solution (n = 18). The gypsum source was flue gas desulfurization gypsum ($CaSO_4{\bullet}H_2O$), which had a purity of 90% (20% Ca and 17% S). Gypsum solutions (EC ≈ 2.26 dS m^{-1}) were prepared by adding 10 g of oven dried (105°C) gypsum to 4-L of degassed DI water, which was then stirred for a period of 1-hr. The Na, K, Mg, and Ca concentrations of the gypsums solutions were 0.42, 0.11, 0.86, and 29.9 $mmol_c$ L^{-1}, respectively.

The wicking treatments were ground wheat straw (n = 12), an engineered paper-based humidifier wick (1043 Super Wick, Essick Air Products, Inc.) (n = 12), and a control which consisted of a bare soil surface (n = 12). The wheat straw (S) was ground and sieved to achieve a size distribution of 1-5 cm in length and packed (30 g) into the soil columns to a depth of 7.5 cm above the soil surface. Humidifier wicks (SW) consisted of multiple sheets of pressed paper fibers glued together and modified to occupy the top 7.5 cm of each soil column. SW treatments were placed directly onto the surface of each soil. Each SW was in contact with approximately 40% of the soil while the other 60% was exposed to the atmosphere. The average mass of each SW treatment was 38 g.

Prior to the initiation of this study, soils were wetted with DI water from the bottom of each column for a period of 21-d, at which point each column had been wetted completely to the surface. Following the initial wetting of the columns, bottles were either refilled with DI water or emptied and filled with the gypsum solution. On day one of the study, each column was connected to a Mariotte siphon containing either DI water or a gypsum solution and assigned one of the three wicking treatments with three reps for each combination of soil, wick, and wetting treatment (n = 36). Soil columns and treatments were organized utilizing a completely random design prior to the initiation of sub-irrigation. The experiment lasted for 56-d and the wicking materials S and SW were removed and replaced every 14-d. The removed wicking materials were immediately weighed with mass recorded, and then allowed to air dry within the greenhouse. To prevent the buildup of air pressure in the head space of the Mariotte siphons, each bottle was wrapped in a water-saturated cotton towel and cooled through evaporative processes. To determine the evaporative loss from each soil column, the initial weight (g) of each bottle was recorded on day one of the study and bottles were subsequently reweighed on a 3-d basis until the conclusion of the experiment. To determine evaporative losses from the soil columns, the sum of the final bottle weights (g) and the water contained in the wicking materials upon removal (g) were subtracted from the initial weights of the Mariotte siphons (g).

Following the cessation of the experiment, soil columns were disconnected from their respective Mariotte siphons and frozen at temperatures of -12ºC for 7-d. Once frozen, columns were dissected into six, 5 cm sections using a reciprocating saw. Soil samples from each column were weighed, air dried, ground to pass a 2-mm sieve, and analyzed at AGVISE Laboratories using the same methodology used to determine the initial soil cation concentrations and EC of the soil solution. Each of the removed wicking materials were washed in 1L of DI water for a 15-min and the extracts were quantified for cations and EC as described above. A mass balance analysis was then conducted to determine the total mass Na reduction (%) from each of the soil columns using Eq. [2].

Statistical Analysis

To determine if the solution type, soil texture, and wicking material influenced the total mass reduction of Na in the soil (%), average EC of the soil solution (dS m^{-1}), and total evaporative loss (mL) from each column over the duration of the experiment, a mixed model analysis of variance was used in SAS with a Tukey's adjustment and significance determined at the 0.05 level of confidence (version 9.4, SAS Institute, Inc.). No reduction in salts occurred in columns with no wicking treatment (i.e. control) and thus these columns were not used in the statistical analysis for the mass reduction of Na (%). The statistical analysis of the average EC of the soil solution was conducted by calculating the difference from the initial and final EC levels for each soil and determined by averaging the values across depth for both the silty clay and loam soils, respectively. To compare the EC of the soil solution and the extractable Na (i.e. %Na) across 5 cm depths, 95% confidence intervals were calculated across depths from the mean values of the replicates for each combination of wick, soil, and solution treatments.

Results and Discussion

Na Removal from the Soil Profile

The effect of wick material (S and SW), solution (gypsum and DI water), soil texture (silty clay and loam), the interaction between soil texture and wick material, and the three way interaction between wick material, solution, and soil texture all had a significant ($p \leq .05$) influence on the total mass reduction of Na (%) in the soil profile as shown in Table 8. Across soil textures and solutions, average Na reductions from soil columns with the SW (57.7%) treatment were significantly greater than those with the S treatment (9.22%) (Table 9). In columns irrigated with the gypsum solution, significantly greater amounts of Na (37.6%) were removed from the soil profile than in the columns irrigated with purified water (29.3%). Across soil textures, significantly greater amounts of Na were removed from the loam soil (52.1%) than the silty clay soil (14.8%). Columns treated with the SW treatment exhibited a significantly greater amount of Na removal from the loam soil when compared to the silty clay soil. A similar relationship between the two soil textures was also found in columns treated with the S.

Table 8: Analysis of variance for electrical conductivity (dS m^{-1}), mass Na reduction in the soil (%), and the cumulative evaporative loss from individual columns.

	Electrical Conductivity (dS m^{-1})[†]				Na Reduction (%)[‡]				Evaporative Losses (mL)[§]			
Effect	Num. DF	Den. DF	F Value	Pr > F	Num. DF	Den. DF	F Value	Pr > F	Num. DF	Den. DF	F Value	Pr > F
Wick	1	14	202.5	<.0001	1	14	462.28	<.0001	2	21	162.01	<.0001
Solution	1	14	1.74	0.2083	1	14	13.83	0.0023	1	21	18.09	0.0004
Soil	1	14	121.8	<.0001	1	14	274.06	<.0001	1	21	29.9	<.0001
Wick*Solution	1	14	1.43	0.2519	1	14	3.48	0.0833	2	21	3.03	0.0696
Wick*Soil	1	14	39.9	<.0001	1	14	109.5	<.0001	2	21	70.84	<.0001
Solution*Soil	1	14	2.08	0.1709	1	14	2.67	0.1244	1	21	0.52	0.478
Wick*Solution*Soil	1	14	0.07	0.7958	1	14	7.34	0.017	2	21	0.28	0.7585

[†] Measured from 1:1 suspensions of distilled water:soil with values averaged across depth for each treated column. Comparison of final and initial EC was conducted utilizing the difference between the initial and final values. Control columns were not included in this analysis.

[‡] Extracted from the exchanger and solution phase using 1:10 soil:1M ammonium acetate. Mass balance of N was conducted using Eq. [2] (Ch. 3). Control columns were not included in this analysis.

[§] The cumulative evaporative loss (mL) from individual columns containing the silty clay soil was determined from the diff. between initial and final bottle weights (assuming that 1 g → is equal to 1 mL) of Mariotte siphons. In columns with the loam soil, the diff. between the initial/final bottle weights and the final mass of water in the soil were used.

Table 9: Descriptive statistics for total mass Na reductions (%) across sub-irrigating solution, wick, and soil textural treatments.

Treatment	N	Max	Min	Mean	SD
Gypsum	12	92.3	2.00	37.6	34.3
DI Water	12	91.1	0.55	29.3	35.4
SW	12	92.3	5.82	57.7	33.5
S	12	26.4	0.55	9.22	8.20
Loam	12	92.3	9.06	52.1	38.0
Silty Clay	12	49.4	0.55	14.8	16.5

In silty clay soils with the SW treatment, significantly greater amounts of Na was removed from the soil profile when the gypsum solution was used for sub-irrigation than in the columns sub-irrigated with DI water (Figure 4). In contrast, no difference in Na removal was exhibited between solutions in the silty clay soils treated with the S treatment. Across columns containing the loam soil, the SW treatment reduced Na concentrations by upwards of 90% for both the gypsum and DI water treatments. Similar to the silty clay soils, columns with the S treatment had relatively low Na removal totals (< 20%) across both solutions. In addition, no significant difference in average Na removal between the solutions was found in the loam soils treated with the S.

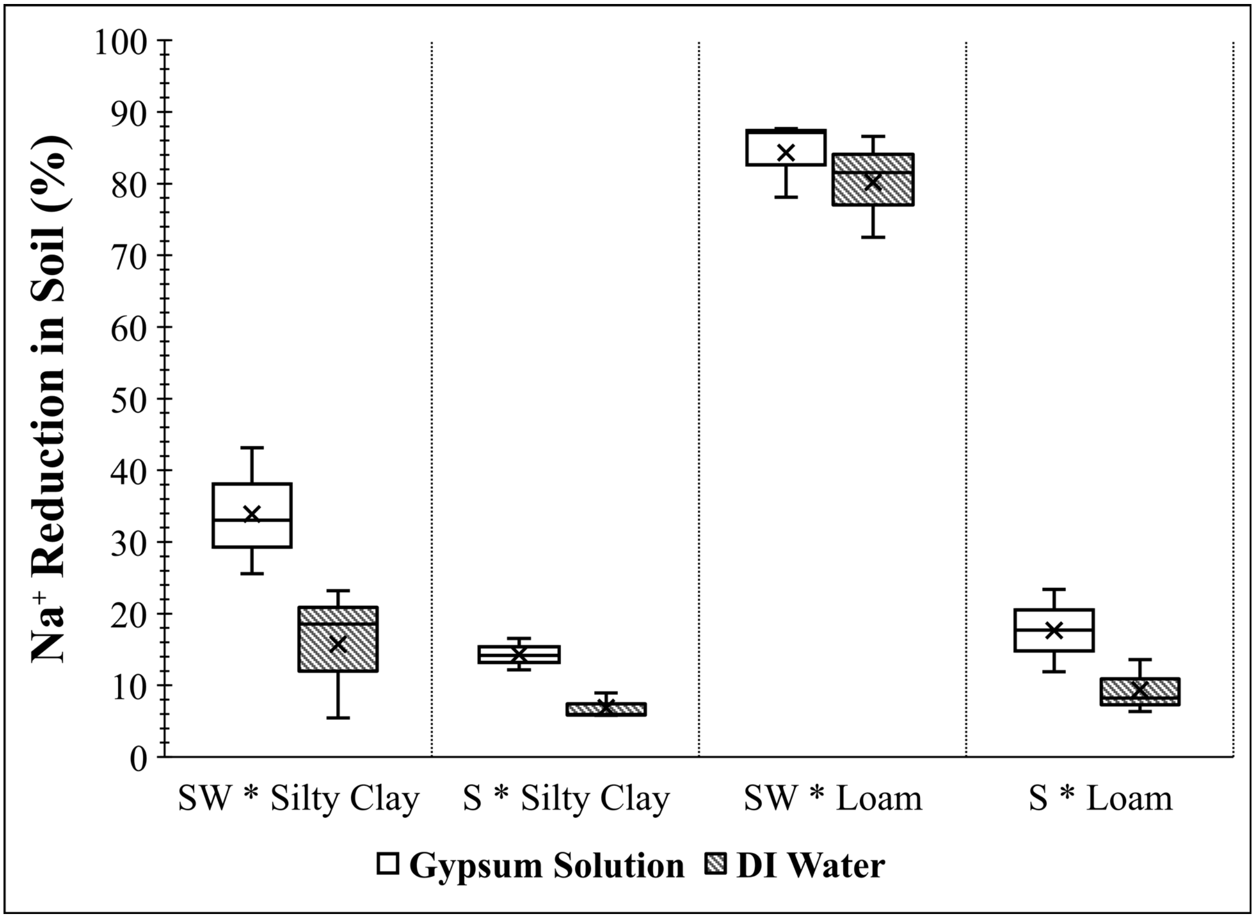

Figure 4: Mass Na reduction (%) in columns containing silty clay and loam soils across wicking materials (super wick, SW; wheat straw, S) and solution types (gypsum solution and distilled, DI, water).

Electrical Conductivity

The difference between the initial and the final EC of the soil solution (i.e. reduction from the initial), averaged across 5 cm depths for each column, was significantly influenced by the wicking material, soil texture, and the interaction between the two (Table 8). On average, the greatest reductions in final EC occurred in soil columns treated with the SW materials (9.7 dS m^{-1}; data not shown). In columns containing the loam soil, the SW treatment resulted in an average reduction in soil EC of 14.4 dS m^{-1}, while the same treatment in columns containing the silty clay soil exhibited reductions of slightly more than 5 dS m^{-1}. Across the two soil textures and solutions used in this study, only modest reductions in average soil EC were observed in columns treated with the S (2.05 dS m^{-1}), which reflects the low amounts of Na removed from the soil profile by this treatment over the duration of the experiment.

In figure 5, the average EC of the soil solution (dS m^{-1}) and the concentrations of extractable Na (%) are shown at incremental depths of 5 cm in columns containing both soil textures and treated with each combination wicking material and sub-irrigating solution. During the 56-d of the experiment, both EC and extractable Na decreased with increasing depth from the soil surface across all treatments. In columns with the silty clay soil, the EC of the soil solution was not significantly different between wick and sub-irrigation treatments at depths of 0-5, 10-15, 20-25, and 25-30 cm (Figure 5). Values of extractable Na across all depth increments were not significantly different across both wick and sub-irrigation treatments. In columns containing the loam soil, the EC of columns treated with the SW and sub-irrigated with gypsum solution were significantly lower than the S treatment in combination with both sub-irrigation treatments at 0-5 and 5-10 cm depths, while at 10-15 and 15-20 cm depths the EC of the SW treated soils were significantly lower than that of the S treated soils. At 20-25 cm depths, the loam soil with the S and gypsum treatments were significantly greater than that of the SW treated soils. No significant difference at 25-30 cm depths was found in EC across treatments in the loam soil. In loam soils, the concentrations of extractable Na (%) across depths of 10-15, 15-20, 20-25, and 25-30 cm were significantly lower in columns treated with the SW in comparison to those treated with the S.

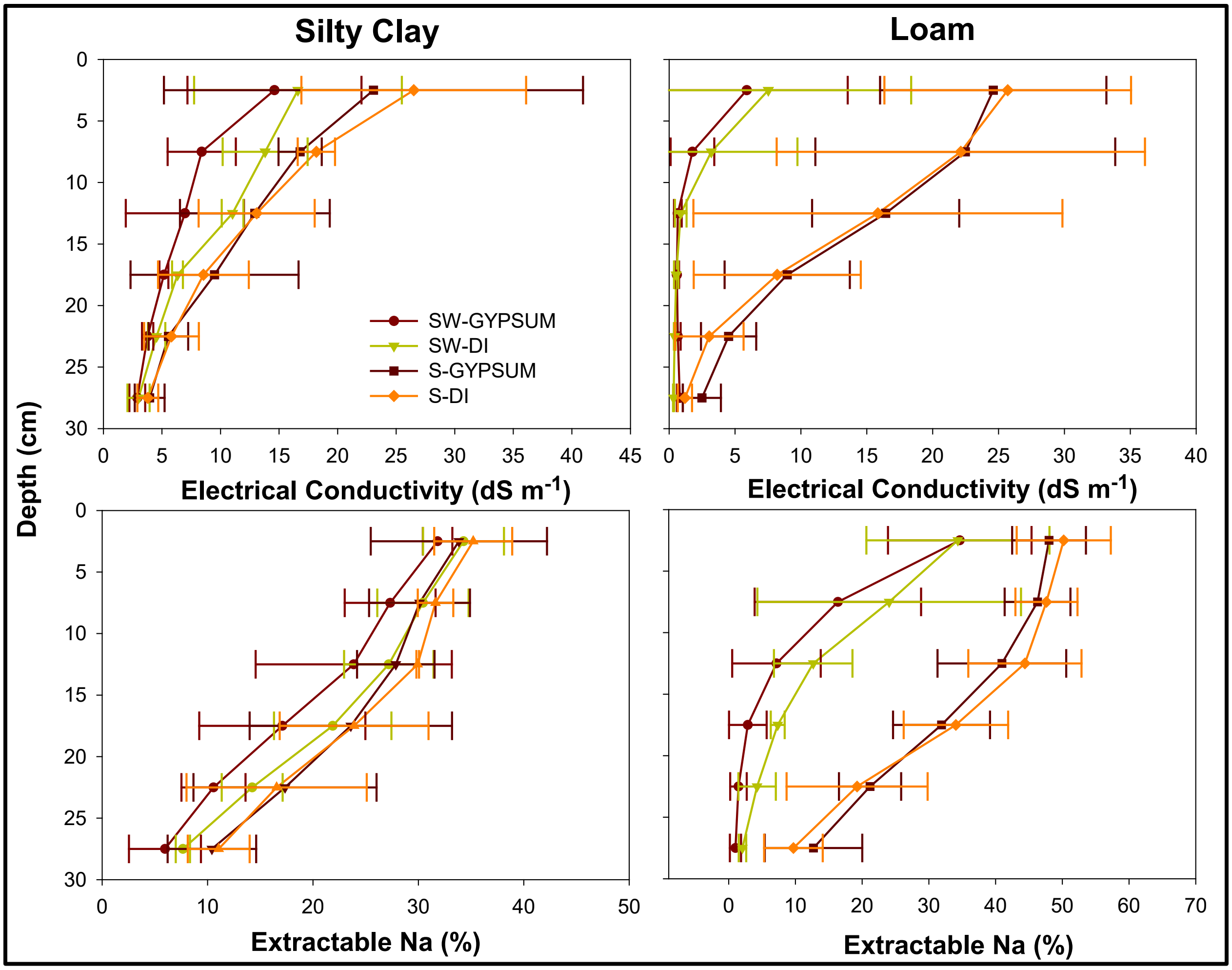

Figure 5: Electrical conductivity (dS m^{-1}) and extractable Na (%) measured at 5 cm depths across silty clay and loam soils treated with every combination of wicking material and solution. Error bars represent the 95% confidence intervals from the mean across replicates for each combination of soil, wicking, and sub-irrigation treatments.

The relationship between the EC of the soil solution and the concentration of Na occupying exchange sites or within the soil solution determines whether structural deterioration caused by swelling or dispersion will occur (DeSutter et al., 2015; Hanor, 2007; Shainberg and Letey, 1984). The specific thresholds of soil EC and extractable Na concentration that determine when these processes begin to materialize varies across soil characteristics; however, the primary determinants include the clay mineralogy of the soil (e.g. kaolinite, smectite, illite), soil texture, the concentration of Na on the exchange sites or within the soil solution, and the EC of the soil solution (He et al., 2013; Marchuk and Rengasamy, 2011; Quirk, 2001; Zhang and Norton, 2002). Through the application of irrigation water exhibiting SAR values of 4 and EC values less than 2 dS m^{-1}, Saurez et al. (2008) observed an overall decline in saturated hydraulic conductivity in a loam soil, indicating that at these EC levels, Na caused clay particles to swell and/or disperse. In suspensions of montmorillonite clays, He et al. (2013) concluded that the dispersion of clay particles could be prevented if the EC of the solution is >6 dS m^{-1} and SAR values are ≤24 or when the EC of the solution was ≥2dS m^{-1} and SAR values were ≤12. To use the thresholds found by both Suarez et al. (2008) and He et al. (2013) for comparison between EC and extractable Na (%) across depth to determine the risk for swelling and dispersion, the $EC_{1:1}$ values in this study were converted to EC_e (solution phase) values using the logarithmic equations developed by Klaustermeier (2016) while the values for extractable Na (%) have previously been shown to be directly correlated to SAR when values are ≤50 (DeSutter et al., 2015; Oster et al., 1999). Across treatments used in this experiment, the highest risk for swelling and/or dispersive behaviors to occur were found in columns containing the loam soil and SW treatment.

Evaporative Losses

The amount of water lost to evaporation from each column was significantly influenced by the wicking material, soil texture, sub-irrigating solution, and the interaction between wicking material and soil texture (Table 8). Over the 56-d of the experiment, the cumulative evaporative loss from the columns with the SW treatment (654 mL) were significantly greater than the control (400 mL), while the evaporative losses from columns containing the S treatment (153 mL) were significantly less across both soil textures and solutions (Table 10). Columns irrigated with the gypsum solution (452 mL) lost much greater amount of water to evaporation than those irrigated with purified water (355 mL). Across the two soil textures, the average evaporative loss from columns containing the loam soil (468 mL) were significantly higher than those of the columns containing the silty clay soil (332 mL). In columns containing the loam soil and the SW treatment (910 mL), the cumulative losses were significantly greater than that of the control columns (387 mL). In contrast, the average losses from the S were significantly less than the control (108 mL). In columns containing the silty clay soil, the evaporative losses with the SW treatment (398 mL) were not significantly different than that of the control (416 mL), while losses from columns with the S treatment were significantly less than the control (197 mL).

Table 10: Descriptive statistics for the evaporative loss from columns across sub-irrigating solution, wick, and soil textural treatments.

Treatment	N[†]	Min	Max	Mean	SD
Gypsum	17	102	1016	452	307
DI Water	18	70.0	874	355	237
Control	11	284	591	400	110
SW	12	290	1016	654	284
S	12	70.0	220	153	50.9
Loam	18	70.0	1016	468	354
Silty Clay	17	179	590	332	126

[†] One column containing the silty clay soil with the control and gypsum treatments was omitted from this analysis due to a persistent leak over the 56-d duration of the experiment.

Relationships between Wick Properties, Na Removal, Solution Type and Soil EC

The effectiveness of the methodology used in this study to 1) remove Na from the soil profile and 2) decrease the EC of the soil solution was dependent on the physical properties of the wicking materials, the texture of the soil, and the ability of the sub-irrigated solutions to facilitate the movement of ions into the wicking medium. The SW treatment consisted of a number of paper-based, fibrous sheets glued together into a rigid design. The intent of this design is to maximize the absorptive capacity of the material as well as its total surface area which, in turn, promotes the rapid evaporation of absorbed water. These characteristics explain why columns treated with the SW material exhibited significantly higher evaporative losses, Na removal totals, and average reductions in soil EC over the course of this study. In contrast, the S treatment (i.e. ground wheat straw) had little pore connectivity between the various strands, which restricted the capillary transport of water upwards towards the evaporative front (Green et al. 2019).

A secondary goal of this study was to determine whether the solution saturated with gypsum would provide an increase in total mass Na removal, promote water movement through the soil, and maintain the average soil EC across depths when compared to columns sub-irrigated with DI water. In the silty clay soil columns treated with the SW material, a significant difference in total mass Na removal (%) was found between the DI water and gypsum sub-irrigation treatments (Figure 4). In this case, it is likely that the Ca provided by the gypsum solution was effective in displacing Na from soil's exchange sites, which in turn allowed Na to be readily translocated upwards into the wicking material. Although a similar relationship was not shown in the data for the silty clay soils treated with the S treatment, it is plausible that the inability of wheat straw to absorb significant quantities of water through the use of either solution confounded the effects of the gypsum in displacing Na from soil's exchange sites. In columns containing the loam soil, no significant difference in Na removal was found between sub-irrigation solutions for both the SW and S treatments. This was most likely due to the coarser texture of the soil and the greater distribution of large pore sizes which, in turn, allowed for a greater amount of solution to pass through the soil over the course of the experiment while removing significant amounts of Na regardless of the solution used for sub-irrigation.

Comparison of Surficial Remediation Techniques

Previous research of surficial remediation techniques for salt-affected soils have relied on the application of a crystallization inhibitor to the soil surface and/or the addition to a wicking medium and have been met with some of measure of success in laboratory settings. Klaustermeier and Daigh (2016) and Klaustermeier et al. (2017) observed reductions in total NaCl concentrations of 46%, 57%, and 29% in sandy loam, loam, and silty clay soils over period of only 7-d, while Angin et al. (2018) noted a similar reduction of 42.9% in a silty clay soil over a period of 14-d. Using the surficial application of a wicking media treated with the crystallization inhibitor potassium ferrocyanide, Swallow and O’Sullivan (2019) observed average reductions in NaCl concentrations of 81% in clay loam soils. Furthermore, a 23% reduction in NaCl concentration was also found using an untreated wicking material over a period of 30-d (Swallow and O’Sullivan, 2019). With the methodology used in this study, the maximum Na reductions from loam soils (89%) exceeded those of similar textured soils that had been treated with a crystallization inhibitor by Klaustermeier and Daigh (2016) and Klaustermeier et al. (2017). On average, the total proportion of Na removed from the columns containing the silty clay soil used in this study (14.8% ± 16.5) were comparable to the findings of Swallow and O’Sullivan (2019), Klaustermeier and Daigh (2016), and Klaustermeier et al. 2017, however the reductions in this experiment were achieved over a much longer duration (56-d).

Wicking Salts: Advantages, Limitations, and Potential for Field Scale Remediation

The use of wicking materials for the remediation of salt-affected soils may provide a number of advantages when compared to conventional (e.g. leaching, dig and haul, phytoremediation, etc.) and contemporary (e.g. crystallization inhibitors) salt removal techniques. In comparison to the conventional practice of applying soil amendments (e.g. gypsum) and large amounts of water to leach Na from the soil profile, the placement of wicking materials into or across the soil surface to accumulate and permanently remove salts would work passively with natural processes such as the capillary rise of soil water and dissolved salts in arid and semi-arid climates. When compared to the ex-situ method of soil excavation and removal (i.e. dig and haul), the use of wicking materials may provide a less expensive and intrusive alternative, while also negating the need to replace the excavated soil with topsoil from another location. Phytoremediation, or the use of salt-tolerant (i.e. halophytic) plants to either bioaccumulate and/or promote the leaching of salts downwards in the soil profile, has been studied by a number of researchers in brine-contaminated soils (Young et al., 2011; Manouski and Kalogerakis, 2011; Keiffer and Ungar, 2002). The effectiveness of using plants for remediation on highly saline soils, however, may have a number of limitations including the uneven establishment and growth of vegetation, the prohibitive amount of time needed to accumulate appreciable amounts of salts, and the lack of availability of halophytic plant species to remediation specialists (Young et al., 2011; Qadir et al., 2007). The use of wicking materials, on the other hand, would be applicable in soils exhibiting varying degrees of salinity and based on the results of this study and that of Green et al. (2019), appreciable reductions in salt concentrations could be achieved in much less time.

The surficial application of crystallization inhibitors has been proven to be both expedient and effective in laboratory settings, however, a number of factors may limit their effectiveness when used as the sole remediation amendment in field settings. Crystallization inhibitors are often only effective for specific salt species such as NaCl (Angin et al., 2018). In their research, Klaustermeier and Daigh (2016) and Klaustermeier et al. (2017) found that the salt removal efficiency of the crystallization inhibitor ferric hexacyanoferrate decreased significantly when the concentration of salts in the soil decreased and when sulfate-based salts were prevalent. Wicking materials, on the other hand, are indiscriminate in their absorption and removal of salt species at varying concentrations. In addition to salt specificity, the surficial application of crystallization inhibitors to large tracts of contaminated land may leave it susceptible to erosional processes from both water and wind. This would require additional measures to be adopted by remediation specialists to prevent the translocation of the inhibitor as well as the resulting salt efflorescence to other locations. In contrast, wicking materials could be placed into rigid columns or applied in mats, thereby providing increased resistance to the effects of erosional processes and weather conditions. There is also the potential that wicking materials could be washed and reused over time, making them a more sustainable option in comparison to crystallization inhibitors.

Before the methodology presented in this study can be applied in field settings, a number of considerations need to first be addressed. The wicking materials used in this study may have limited applicability in field settings due to practicality. To make the application of this method feasible in field settings, wicking materials need to be identified that are both effective in accumulating salts and durable enough to withstand weather conditions. The ideal material would have physical properties similar to those exhibited by the SW material including a high surface area, large absorption capacity, high porosity, and structural rigidity. In addition, this material would need to be readily available to remediation specialists at costs low enough to justify the use of this method over other, more expedient methods such as dig and haul.

The mass of salts removed from the soil columns used in this study were closely tied to the ability of wicking materials to pull water from the soil through capillary suction. As soils dry, the matric potential of the soil matrix becomes increasingly negative to a point where wicking materials would no longer be able to effectively absorb soil water and remove salts. In consequence, the effectiveness of this method in arid and semi-arid environments may be limited unless the contaminated soil is irrigated, or a shallow water table is present to maintain hydraulic contact between the soil and wicking material. Further research needs that are required before this method can be used commercially in field settings include the determination of 1) the most effective placement of wicking materials in field conditions to maximize salt uptake, 2) the cost-benefit relationship of this method compared to other conventional methods, and 3) the applicability of this method for larger spill sites.

Conclusions

In this study, it was shown that significant amounts of Na can be removed from brine-contaminated soils through the application of highly absorbent wicking materials on the soil surface given that soil water contents are sufficient to maintain hydraulic contact with the wicking materials. In soils with silty clay and loam textures, wicking materials reduced Na concentrations upwards of 38.4 and 89.5%, respectively. On average, the use of a gypsum solution to sub-irrigate brine-contaminated, silty clay soils significantly increased the amount of Na removed by the wicking material SW over the 56-d experiment. In comparison to other contemporary remediation techniques that utilize crystallization inhibitors to effloresce salts above the soil surface, this method achieved similar reductions, however, these reductions occurred over a much longer time period. The potential advantages of using manufactured wicking materials for salt removal over other methods include, low energy input, minimal disturbance to the soil profile, the permanent removal of salts, the potential for reuse of materials, and its applicability in sensitive environments such as wetlands. Further research is needed to determine the effectiveness of this method in field scale trials.

References

Angin, I., Sari, S., Lutfi Aksakal, E., & F. Tohumcu. 2018. The use of iron (III) ferrocyanide soil amendment for removing salt from the soil surface. Arid Land Res. and Manage. 1-6.

Clark, C. and J. Veil. 2009. Produced water volumes and management practices in the United States. Argonne National Lab., Argonne, IL, United States. doi:10.2172/1007397.

Daigh, A. L., & Klaustermeier, A. W. 2016. Approaching brine spill remediation from the surface: a new in situ method. Agri. Environ. Lett. 1:150013.

DeSutter, T., D. Franzen, Y. He, A. Wick, J. Lee, B. Deutsch, and D. Clay. 2015. Relating sodium percentage to sodium adsorption ratio and its utility in the Northern Great Plains. Soil Sci. Soc. of Am. J. 79(4): 1261-1264.

Gleason, R.A., T.L.C. Chesley-Preston, J.L. Coleman Jr., S.S. Haines, K.E. Jenni, T.L. Nieman, Z.E. Peterman, M.P. van der Burg, T.M. Preston, B.D. Smith, B.A. Tangen, and J.N. Thamke. 2014. Brine contamination to aquatic resources from oil and gas development in the Williston Basin, United States. No. 2014-5017. US Geological Survey. doi:10.3133/sir20145017.

Green, A.W., DeSutter, T.M., Daigh, A.L.M, and M.A. Meehan. 2019. Wicking salts from brine-contaminated soils: a potential method for in-situ remediation. Agric. Environ. Lett. doi:10.2134/ael2018.12.0069.

Guerra, K., K. Dahm and S. Dundorf. 2011. Oil and gas produced water management and beneficial use in the Western United States. US Department of the Interior, Bureau of Reclamation.

Hanor, J.S. 2007. Variation in the composition and partitioning of adsorbed cations at a brine-contaminated crude oil production facility in southeastern Louisiana, USA. Appl. Geochem. 22: 2115-2124.

Harris, T.M., J. Bryan Tapp and K.L. Sublette. 2005. Remediation of oil-field brine-impacted soil using a subsurface drainage system and hay. Environ. Geosci. 12: 101-113.

He, Y., DeSutter, T. M., & Clay, D. E. 2013. Dispersion of pure clay minerals as influenced by calcium/magnesium ratios, sodium adsorption ratio, and electrical conductivity. Soil Sci. Soc. Am. J., 77(6), 2014-2019.

Keiffer, C.H. and I.A. Ungar. 2002. Germination and establishment of halophytes on brine-affected soils. J. Appl. Ecol. 39: 402-415.

Klaustermeier, A.W. 2016. Brine-Contaminated Soils in Western North Dakota: Site Assessment Methodology and a New In-Situ Remediation Method. M.S. Thesis, Dept. of Soil Science, North Dakota State University, Fargo, ND. p. 47.

Klaustermeier, A.W., A.L. Daigh, R.F. Limb and K. Sedivec. 2017. Crystallization inhibitors and their remediation potential on brine-contaminated soils. Vadose Zone J. 16(4). doi:10.2136/vzj2016.10.0095.

Manousaki, E. and N. Kalogerakis. 2011. Halophytes—an emerging trend in phytoremediation. Int. J. of Phytorem. 13: 959-969.

Marchuk, A. and P. Rengasamy. 2011. Clay behavior in suspension is related to the ionicity of clay–cation bonds. Appl. Clay Sci. 53: 754-759.

Murphy, E.C., A.E. Kehew, G.H. Groenewold and W.A. Beal. 1988. Leachate generated by an oil-and-gas brine pond site in North Dakota. Groundwater. 26: 31-38.

Oster, J.D., I. Shainberg, and I.P. Abrol. 1999. Reclamation of salt-affected soils. Agricultural drainage. Agron. Monogr. 38. ASA, CSSA, SSSA, Madison, WI.

Qadir, M., J. Oster, S. Schubert, A. Noble and K. Sahrawat. 2007. Phytoremediation of sodic and saline-sodic soils. Adv. Agron. 96: 197-247.

Quirk, J.P. 2001. The significance of the threshold and turbidity concentrations in relation to sodicity and microstructure. Aust. J. Soil Res. 39: 1185-1217.

Rengasamy, P., Greene, R. S. B., & Ford, G. W. 1986. Influence of magnesium on aggregate stability in sodic red-brown earths. Aust. J. Soil Res. 24(2): 229-237.

Shainberg, I. & J. Letey. 1984. Response of Soils to Sodic and Saline Conditions. Hilgardia. 52: 1-57. doi: 10.3733/hilg.v52n02p057.

Suarez D.L., J.D. Wood, and S.M. Lesch. 2008. Infiltration into cropped soils: effect of rain and sodium adsorption ratio – impacted irrigation water. J Environ. Qual. 37: S169–S179.

Swallow, M., and G. O'Sullivan. 2019. Biomimicry of vascular plants as a means of saline soil remediation. Sci. Total Environ. 655: 84-91.

Thimm, H.R. 1990. The prevention of resalinization in the reclamation of saltwater spill sites. J. of Canadian Petroleum Tech. 29(4).

Young, M.A., D.G. Rancier, J.L. Roy, S.R. Lunn, S.A. Armstrong and J.V. Headley. 2011. Seeding conditions of the halophyte Atriplex patula for optimal growth on a salt impacted site. Int. J. Phytorem. 13: 674-680.

Zhang, X.C., and L.D. Norton. 2002. Effect of exchangeable Mg on saturated hydraulic conductivity, disaggregation and clay dispersion of disturbed soils. J. Hydrol. 260: 194–205. doi:10.1016/S0022-1694(01)00612-6

GENERAL CONCLUSIONS

The first objective of this research was to determine the germination thresholds of four crop and graminoid species in the presence of brine and NaCl solutions at increasing levels of electrical conductivity (EC). Across the eight plant species tested in this research, *Hordeum vulgare* (barley), *Helianthus annus* (sunflower), *Beta vulgaris* (sugar beet), *Pascopyrum smithii* (western wheatgrass), *Elymus hoffmannii* (AC Saltlander), *Leymus triticoides* (beardless wildrye)*,* and *Elymus trachycaulus* (slender wheatgrass) exhibited no significant difference in final germination between NaCl and brine solutions at increasing levels of salinity, indicating that previously established salt-tolerance thresholds for these species in NaCl-dominated environments can be accurately applied for determining their suitability in brine-contaminated environments. In addition, AC Saltlander and western wheatgrass exhibited statistically greater rates of germination than the other species tested in this study at EC levels above 24 dS m^{-1}, making them the most desirable species for revegetation efforts in brine-contaminated soils.

The second objective of this research was to determine the remediation potential of using the surficial application of wicking materials to absorb and remove salts from brine-contaminated soils. In a preliminary study, significant mass reductions of Na in sandy loam, brine-contaminated soils were achieved using Second Nature® Wood Fiber Plus Hydraulic Mulch (Profile Products®), 1043 Super Wick (Essick Air Products, Inc.), and CBW9 Humidi-Wick (BestAir Pro®) as wicking materials. In a second study utilizing a similar methodology, the 1043 Super Wick reduced Na concentrations in brine-contaminated silty clay and loam soils by upwards of 38.4 and 89.5%, respectively. In addition, it was found that the use of a gypsum solution to sub-irrigate the silty clay soil significantly increased the amount of Na removed by the 1043 Super Wick over the course of the experiment. The results of these studies indicate that further research in field-scale trials is warranted. In addition, this method may provide a more permanent means of salt-removal in brine-contaminated environments than conventional ex-situ and in-situ remediation methods.