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July 15, 2016

Ms. Karlene Fine
Executive Director
North Dakota Industrial Commission (NDIC)
600 East Boulevard Avenue, Department 405
State Capitol, 14th Floor
Bismarck, ND 58505-0840

Dear Ms. Fine:

Subject: Quarterly Progress Report for the Period of April 1 – June 30, 2016, Entitled "Program to Determine the Uniqueness of Three Forks Bench Reserves, Determine Optimal Well Density in the Bakken Pool, and Optimize Bakken Production"
Contract No. G-030-060; EERC Fund 18776

Enclosed please find the Energy & Environmental Research Center (EERC) Quarterly Progress Report for the subject project, also known as the Bakken Production Optimization Program. If you have any questions, please contact me by phone at (701) 777-5157 or by e-mail at jharju@undeerc.org.

Sincerely,

Gary C Almlie

for John A. Harju
Vice President for Strategic Partnerships

JAH/rlo

Enclosure

E-Mailed Report Only: Brent Brannan, NDIC Oil and Gas Research Council
Lynn Helms, NDIC Department of Mineral Resources, Oil and Gas Division
Ron Ness, North Dakota Petroleum Council

PROGRAM TO DETERMINE THE UNIQUENESS OF THREE FORKS BENCH RESERVES, DETERMINE OPTIMAL WELL DENSITY IN THE BAKKEN POOL, AND OPTIMIZE BAKKEN PRODUCTION (BAKKEN PRODUCTION OPTIMIZATION PROGRAM)

QUARTERLY PROGRESS REPORT
April – June 2016

BACKGROUND

The goal of the Bakken Production Optimization Program (BPOP) being conducted by the Energy & Environmental Research Center (EERC) in close coordination with Continental Resources, Inc. (Continental) and several of the Williston Basin's other premier operating companies is to simultaneously improve Bakken system oil recovery while reducing its environmental footprint. The program is investigating new technologies and approaches to simultaneously increase the understanding of potential petroleum reserves in the Bakken–Three Forks system and decrease recovery costs in an environmentally sound manner.

The anticipated outcomes of BPOP are to increase the well productivity and economic output of North Dakota's oil and gas resources, decrease environmental impacts of wellsite operations, and reduce demand for infrastructure construction and maintenance. Specific results will include a) a greater understanding of Bakken–Three Forks reservoirs and subsequent significant increases to estimates of recoverable hydrocarbons; b) less truck traffic, resulting in decreased diesel emissions, road dust, and spills; c) reduced road maintenance costs, wastewater production, disposal costs, and freshwater use; d) reduced land use impacts; and e) increased revenue for the state, royalty owners, and operators from added product streams captured earlier in the well life cycle.

The following quarterly report summarizes the program activities from April through June 2016.

ACCOMPLISHMENTS DURING REPORTING PERIOD

Continental leads Phases I–IV. The EERC leads activities in Phase V.

Phases I–IV (Continental)

- No activity occurred during this reporting period.

Phase V – Optimization of Wellsite Operations (EERC)

Hydrocarbon Utilization (EERC Task 1)

Flaring Reduction

- North Dakota Petroleum Council (NDPC) Flaring Task Force/database development.
  - The EERC continued to work with technology/service providers capable of utilizing associated gas upstream of traditional gas-gathering and processing infrastructure and gathered information describing their remote capture offerings. To date, 70 companies have provided company and technical information to the database. Approximately 20% of them have had systems deployed in North Dakota.
  - The Flaring Solutions Web site has been changed to simplify navigation. It is now possible to access flaring-related documents, review company information within the database, or add technologies to the database from one location: www.undeerc.org/Flaring_Solutions.
  - The EERC continued to review technical data provided by vendors and is supporting ongoing vendor efforts to develop offerings that address the challenges leading to gas flaring.
  - The EERC continued to work with producers and vendors to identify opportunities for demonstration projects that have the potential to improve gas utilization and reduce the risk of implementing new technologies and strategies. Work continues to assess the relative impact that individual technologies can have on gas use, thereby decreasing the fraction of flared gas in North Dakota.

Fugitive Gas Emissions

- Fugitive emissions reduction from production facilities has become an important topic for North Dakota producers. To support BPOP members, the EERC has initiated work to better define existing and emerging regulatory requirements and assess opportunities to reduce emissions.

- Work has begun on the preparation of a Bakken Smart fact sheet on fugitive emissions. A final document will be completed soon and submitted with the next quarterly report.

- Federal and state regulations relevant to fugitive emissions are being reviewed, and a summary of key requirements is being prepared. The EERC will work with BPOP members and develop a summary document with the format and content that is useful to industry as they work to improve facility performance.

- An EERC representative attended the Leak Detection and Repair Conference in Denver, Colorado.

Investigation of Rich Gas for Enhanced Oil Recovery (EOR)

- Several experiments were conducted to determine the potential for utilizing ethane as an injectant for EOR in the Bakken. Tests included measuring multiple-contact minimum miscibility pressure (MMP) under Bakken reservoir conditions, evaluating Bakken crude oil that mobilized into the upper "miscible" phase during MMP tests, and exposing rock samples to ethane to determine the rate of crude oil recovery from untreated Bakken rocks. Results from these tests have been described in a summary report included as Appendix A of this quarterly report.

- A preliminary EOR model was developed to compare CO_2 to ethane for EOR. Results indicate ethane could provide superior recovery response compared to pure CO_2 injection. Data generated by this model may provide a basis for further investigation of ethane as an EOR fluid. Results from this modeling exercise have been reviewed, and additional analysis has been ongoing. A summary report will be prepared and provided with the next quarterly report.

Produced Fluids Characterization

- A critical component of Bakken production optimization is a good understanding of produced fluid characteristics and properties. To support subsequent program activities related to maximizing oil recovery, improving facilities operation, and minimizing the environmental footprint of oil and gas production in North Dakota, the EERC has begun developing a database of fluids data. Initial efforts have focused on gathering available gas, oil, and produced water data and identifying data gaps.

Investigation of Oil Compositional Analysis for Source Determination

- Qualitative analyses of Middle Bakken, upper shale, and lower shale rock samples show that aromatic hydrocarbons are much more prevalent in the upper and lower shales than in the Middle Bakken. These initial observations have significant implications ranging from increasing oil production over the life of a well to increasing our understanding of oil maturation and migration in the Bakken (and Three Forks) petroleum systems.

- Laboratory work and method development have begun, with the analyses of several samples that represent the range of thermal maturities (and locations) throughout the Bakken play.

Facilities Process Modeling

- The goals of reduced flaring, lowering crude oil volatility, and eliminating fugitive gas emissions from tanks are often competing, necessitating a thorough systems analysis of production facilities design and operation. To support BPOP members' efforts to improve production facility performance, reduce adverse environmental impacts, and ensure regulatory compliance, the EERC has begun to develop a facilities process model that can be used to simulate different design configurations and operating conditions.

  - Model development began with evaluating process-modeling options and collecting public information regarding site configuration, equipment details, and stream composition data. Steady-state process modeling with Aspen HYSYS was chosen as the initial investigation tool to identify mechanisms that could interfere with fugitive emissions compliance.

  - Other tools such as dynamic process modeling or detailed equipment analysis with finite element modeling were also considered and might be appropriate in the future depending on the issues that are identified.

  - Steady-state modeling was able to reproduce high-level performance trends of gas–oil separation and oil vapor pressure sensitivity by adjusting model input parameters.

  - These exercises were used to identify the process details that will be necessary for the model to achieve predictive capability. These data needs have been summarized, and plans are under way to gather information from industry stakeholders.

Reservoir Performance Modeling

- The main objectives of this activity are to review Bakken production data, select a representative and diverse sample set of 200 wells and create rate-time analysis plots for the sample set, also evaluate production decline and forecast estimated ultimate recovery (EUR). The analysis results will be inspected by groups (e.g., county, field, age and length of completion, etc.) to create time-zero rate-time plots for selected groups for use as a proxy for future well performance. The final task will be to perform simulation studies to replicate the selected time zero performance plots as well as sensitivity cases to test long-term performance impact of different operating conditions.

- Data from about 600 wells that have been producing in McKenzie, Williams, Mountrail, and Dunn Counties in the Bakken Shale were collected, including production, location, field, spud year, length of completion, and number of fracture stages. Approximately 150 wells from each county were selected, which have at least 24-month production data. Well and production data were gathered from the North Dakota Oil and Gas Commission, a public domain that provides only monthly data.

  - After reviewing the production data for these 600 wells, it was decided to focus on a total of 200 wells to evaluate well performance and decline curve analysis. To be more representative and diverse, equal numbers of wells from each production year (pre-2007, 2007, 2008, 2009... 2014) were used. Wells whose production data clearly indicated that they have been restimulated or that have proceeded with workover were eliminated.

  - For the selected wells, production data using the Fetkovich Typecurve method were analyzed to identify the flow regime, whether a well is in transient flow or boundary-dominated flow (BDF). Because no pressure data are available, constant bottomhole pressure was assumed.

  - Analysis results show that many of the selected 200 wells are in BDF. Since the wells are in BDF, using the traditional Arps method will provide an accurate decline curve analysis and forecast of EUR.

  - EERC staff completed creating the rate-cumulative and rate-time analyses plots for decline curve analyses and started inspecting them by groups in order to generate proxies for new well performance.

Waste Management (EERC Task 2)

- No activity occurred during this reporting period.

Water Management (EERC Task 3)

Bakken Water Opportunities Assessment

- No activity occurred during this reporting period.

Inyan Kara Modeling

- Work continued on development of the geologic model of the Inyan Kara Formation.

  - After reviewing the location of saltwater disposal (SWD) wells in more detail, the modeling team decided to extend the finer-scale modeling area approximately 10 miles to the east to encompass a number of disposal wells that occur along the Nesson Anticline and border the western edge of the Fort Berthold Reservation. This increased the aerial extent of the fine-scale geologic model from 2050 square miles to 2400 square miles (Figure 1).

  - This will also extend the area for which model simulations will be conducted to estimate long-term injection capacity and to identify local and regional pressure effects. The grid sizing in the model is 500 meters in both the X and Y directions, and there are a total of 44 layers in the vertical direction, 40 of which occur in the Inyan Kara Formation. For simplicity, the lithologies represented by the layers include clean sand, silty sand, and shale.

- Additional work on this effort focuses on evaluating the utility of Hall plots to identify wells that are already experiencing pressurization/injectivity issues and to estimate the remaining injection volume for each well before pressurization issues may start to develop.

  - Hall plots compare variations in slope of the cumulative injection pressure vs. cumulative injection volume as a means to assess well performance and to provide information on average well injectivity, mean ambient reservoir pressure, and change in properties due to stimulation or formation damage.

  - Hall plots will be created and analyzed for approximately 500 SWD wells in the Bakken region after the methodology and its utility are tested on a small subset of wells.

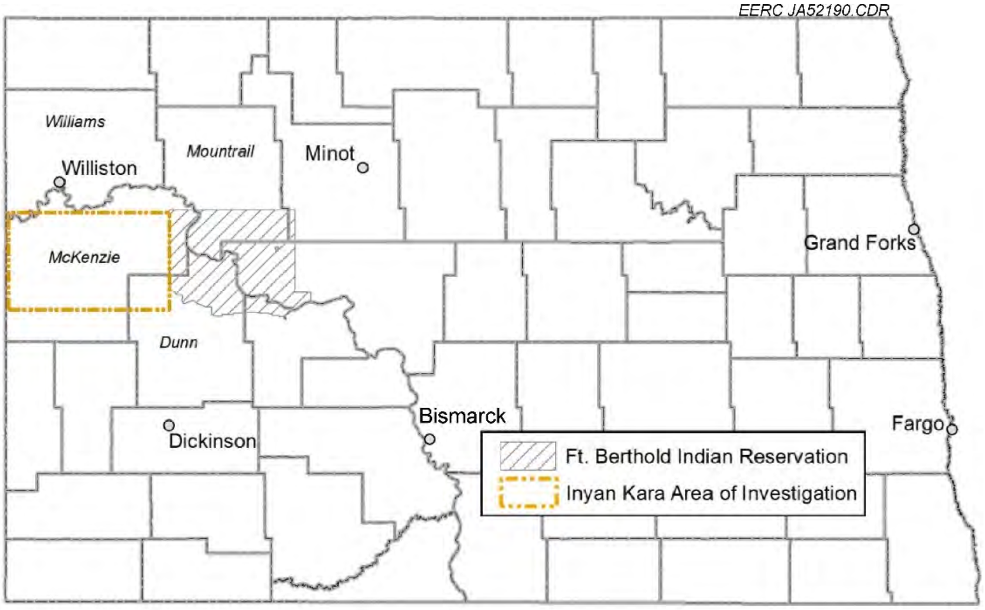

Figure 1. Areal extent of the fine-scale Inyan Kara geologic model.

Site Logistics (EERC Task 4)

- No activity occurred during this reporting period.

Process Optimization and System Failure Analysis (EERC Task 5)

Sucker Rod Premature Deterioration

- EERC staff are investigating premature deterioration of plastic sucker rod guides experienced by several member companies. Several sample rod guides have been received and are being studied for indicators of root cause of premature deterioration. During initial testing, several properties of the four materials will be measured.
    - Mechanical testing will involve measuring the tensile strain versus stress behavior at reservoir temperature.
    - Scanning electron and optical microscopy of surfaces and cross sections will be used to document physical and chemical differences between the new materials and changes caused by exposure to downhole conditions.
    - X-ray diffraction will be used to determine differences in crystallinity between the new materials and changes caused by exposure.
    - Differential scanning calorimetry will be used to determine the glass transition temperatures of the materials because extended use above this temperature can cause material degradation.

  - Other possible tests could include pycnometry to determine the porosity of exposed and unexposed samples and organic extractions of plasticizers to determine if different plasticizers are used between manufacturing lots.

- Results of initial testing will determine the course for subsequent testing, as described in the Future Activities section of this quarterly report.

Waste Minimization and Utilization (EERC Task 6)

- No activity occurred during this reporting period.

Spill Remediation (EERC Task 7)

- EERC staff have continued their involvement with the NDPC Saltwater Spills Task Force, led by BPOP members Oasis Petroleum Company (Oasis), Continental, Hess Corporation (Hess), XTO Energy Company, and Whiting Petroleum Corporation (Whiting), to provide technical documents establishing best practices for mitigating brine and hydrocarbon spills. In collaboration with these BPOP members, the EERC continued to work through the last minor details to complete the North Dakota Remediation Resource Manual. Plans for release are being finalized by the Saltwater Spills Task Force, largely directed by BPOP members.

Land Reclamation (EERC Task 8)

- North Dakota State University's Range Science and Soil Science programs provided final reports on four individual segments of work performed during the past 2 years. These reports are attached as Appendixes B–E in this quarterly report.

Program Management and Development

- At the contractual end of this program (June 30, 2016), a number of late-breaking priorities were presented to the program. A no-cost extension has been requested and granted to permit the EERC to conclude ongoing activities during calendar year 2016. A full technical report on all program activities will be provided to the North Dakota Industrial Commission (NDIC) and all industry partners by January 31, 2017.

- Simultaneously, several program members encouraged the EERC to seek a second period of performance of the program. A proposal for BPOP 2.0 was therefore submitted to NDIC's Oil and Gas Research Program (OGRP) in June 2016. If approved for funding by NDIC, this program extension will continue the type of state–industry collaborative efforts advanced under the current period of performance for an additional 3 years. Industry cost share in excess of OGRP minimum guidelines has been provided, but additional industry cost share will be sought as oil prices rebound.

- EERC staff attended the Interstate Oil and Gas Compact Commission Annual Meeting in Denver, Colorado, May 15–17 to gain general information relevant to BPOP.

- EERC staff attended the NDIC meeting on May 23 in support of discussions to advance the possibility of BPOP 2.0.

- EERC staff attended the Williston Basin Petroleum Conference to support ongoing activities and share information with state and industry representatives.

MEMBERSHIP AND FINANCIAL INFORMATION

BPOP is sponsored by the NDIC Oil and Gas Research Council, Continental, and a consortium of Bakken producers and service companies. Table 1 presents the current budget for this program. Continental's expected in-kind contribution over the project duration is $106,030,000.[1] The anticipated contribution from other industry sponsors is $750,000 a year for a total of $2,250,000. Payments totaling $1,500,000 have been received from all members for Years 1 and 2. It is expected that equal payments will be provided by the industry partners in Year 3. Reminders were provided to those with outstanding invoices during this quarter.

Table 1. BPOP – Expected Budget

Sponsors	**Y1**	**Y2**	**Y3**	**Total**
NDIC Share – Cash*	$3,134,512	$3,204,944	$2,215,044	**$8,554,500**
Industry Share – Cash (confirmed participation)	$750,000	$750,000	$750,000	**$2,250,000**
Continental Share – In-Kind	$40,989,233	$40,989,233	$24,051,534	**$106,030,000**
Total	**$44,873,745**	**$44,944,177**	**$27,016,578**	**$116,834,500**

* Includes $6.26M subcontract to Continental.

Expenses to date by funding source are listed in Table 2. Continental reported an additional $13,874 in noncash cost share during the reporting period. This figure resulted from end-of-project accounting adjustments and reflects Continental's end-of-project accounting of project costs.

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[1] No additional cost-share reporting is expected from Continental for this project. The final cost-share total is approximately $6.9 million less than what was projected at the start of the project. This differential is largely attributed to actual expenditures coming in slightly lower than original estimates. The differential amounts to 6.4% variance, which may be considered within expectations for a project of this magnitude.

Table 2. BPOP – Expenses to Date

	Funding Source		
	NDIC	Industry	Total
EERC	$1,890,404	$1,384,746	$3,275,150
Continental – Subcontract*	$6,260,000		$6,260,000
Continental – In-Kind**		$99,166,805	$99,166,805
Total	**$8,150,404**	**$100,551,551**	**$108,701,955**

* Invoiced to the EERC.
** Reported to the EERC.

FUTURE ACTIVITIES

The planned activities for the next quarter are detailed below.

Phases I–IV (Continental)

- No further work is planned. Phases I–IV are now complete.

Phase V (EERC)

Hydrocarbon Utilization (Task 1)

Flaring Reduction

- The EERC will continue working with vendors to identify opportunities to deploy technology and/or services that match the needs of producers in their efforts to improve gas capture and utilization.

- The EERC will continue working with industry partners and vendors to identify opportunities to conduct demonstration projects that allow stakeholders the ability to evaluate technologies capable of improving gas use.

- The EERC will continue to monitor industry's progress toward meeting the gas capture targets in North Dakota and continue to assess the technical and economic viability of remote capture use.

Minimization of Fugitive Associated Gas Emissions

- A final Bakken Smart fact sheet will be prepared and available for public release. Additionally, work will continue on the creation of a summary document describing fugitive emission regulations relevant to BPOP members.

Investigation of Rich Gas for EOR

- Modeling of ethane as an EOR fluid will be completed next quarter, and results will be reviewed and compiled into a summary report.

Produced Fluids Characterization

- In the upcoming months, the EERC will develop a plan to create a more complete and comprehensive database of fluids properties that can be used by BPOP members and the EERC to enhance production optimization efforts. The plan may form the basis for future work under the proposed BPOP 2.0.

Investigation of Oil Compositional Analysis for Source Determination

- The EERC will obtain several rock samples from up to nine wells located in a range of thermal maturity zones in the Bakken reservoir. For each well, samples of lower and upper Bakken shales will be obtained along with samples of the laminated Middle Bakken (MB3) that is the zone typically targeted for oil production. In addition, samples from some wells will include all relevant lithofacies including MB1 to MB5 and the Three Forks Formation.

- Samples will be solvent-extracted to recover the crude oil, and the crude oil extracts will undergo semiquantitative analysis using high-resolution gas chromatography coupled with mass spectral detection (GC/MS). Analysis will focus on determining the relative amounts of aromatic and aliphatic hydrocarbons in each well and each lithofacie. The results of these analyses, which will be completed in August or early September 2016, will allow us to determine if the initial observations described previously apply across the Bakken reservoir. If the results are positive, subsequent studies will focus on the development and implementation of a formal analytical method (rather than the semiquantitative approach used to date), and its application to further characterize and exploit the use of these "tracer" organics for a better understanding of the reservoir and how they can be used to enhance recoveries.

Facilities Process Modeling

- Data gathering will continue to improve the fidelity of the process model, and a draft model will be completed. The model may be available for subsequent process simulation work under the proposed BPOP 2.0.

Reservoir Performance Modeling

- Simulation studies will be conducted to evaluate reservoir performance, and results will be compiled and analyzed for preparation of a summary report.

Waste Management (Task 2)

NORM Waste Disposal

- No activity is anticipated on this topic during the coming quarter.

Wellsite Waste Assessment

- No activity is anticipated on this topic during the coming quarter.

Water Management (Task 3)

Bakken Water Opportunities Assessment

- North Dakota's Energy Development and Transmission Committee (EDTC) has asked the EERC to present the findings of the "Bakken Water Management Practices and Future Outlook" report at its meeting in Bismarck, which will likely be held in August.

Inyan Kara Modeling

- The EERC anticipates completion of the geologic model for this effort.

- Work will begin on numerical simulation of potential future injection scenarios.

  - Two to three future injection scenarios will be evaluated. One of those scenarios will include the "business as usual" case where the existing SWD wells in the modeled area will continue to inject at the current rate for the next 10, 20, and 30 years in an attempt to identify areas where injection may become problematic or, conversely, where favorable locations for long-term injection exist.

- Work will also continue to determine if Hall plots are an accurate method to assess the long-term injection capacity of individual SWD wells in western North Dakota.

Site Logistics (Task 4)

- No activity is currently planned in this area during the coming quarter.

Process Optimization and Systems Failure Analysis (Task 5)

Sucker Rod Premature Deterioration

- Guided by initial results, EERC staff anticipate completion of a second round of analysis of failing sucker rod guides. This subsequent testing will tentatively include:

  - Longer-term exposure testing of different versions of the plastic rod guides to fluids at temperature and pressure to determine relative rates of changes of properties and, possibly, the mechanism of degradation.

  - Design and employment of an erosion-testing system for long-term exposure tests under downhole conditions to determine the relative erosion resistance of different new materials.

  - Direct collaboration with the plastic suppliers to determine typical testing protocols and to discuss theories explaining rod guide failures.

Waste Minimization and Utilization (Task 6)

- No activity is currently planned in this area during the coming quarter.

Spill Remediation (Task 7)

- The EERC, along with BPOP members, will attend a meeting of the entire Saltwater Remediation Task Force to be held at the North Dakota Department of Health (NDDH) office on August 2, 2016. The agenda for this meeting is to discuss and finalize the NDDH saltwater remediation guidance document and present the final version of the EERC–BPOP Remediation Resource Manual.

Land Reclamation (Task 8)

- The North Dakota Remediation Resource Manual is planned for release during the third quarter of 2016.

Program Development and Management

- During the coming reporting period, the EERC expects to complete all ongoing activities and begin compiling the final technical report summarizing the accomplishments of the program over the past 3 years.

- The EERC will present a summary of the proposal to extend the program for another 3 years to OGRP at a time of OGRP's choosing.

- The EERC will continue to serve in a collaborative capacity for industry and state entities as decisions are made regarding recommendations for alterations of existing heel/toe offsets and along parallel spacing unit boundaries.

APPENDIX A

RAPID AND SIMPLE CAPILLARY-RISE/ VANISHING INTERFACIAL TENSION METHOD TO DETERMINE CRUDE OIL MINIMUM MISCIBILITY PRESSURE: PURE AND MIXED CO_2, METHANE, AND ETHANE

Rapid and Simple Capillary-Rise/Vanishing Interfacial Tension Method to Determine Crude Oil Minimum Miscibility Pressure: Pure and Mixed CO_2, Methane, and Ethane

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ABSTRACT: We report here a simplification of the capillary-rise/vanishing interfacial tension (IFT) method to measure minimum miscibility pressure (MMP) based on only requiring knowledge of when the interfacial tension approaches zero. Simply measuring the height of the crude oil in a capillary at several pressures from ambient to near the MMP pressure and extrapolating the oil height vs. pressure plot to zero oil height yields the MMP without the need of the additional instrumentation and labor required to perform actual IFT measurements. Two to four MMP values can be determined per day with only one experimental apparatus, and the method greatly reduces the initial cost and complexity of the required instrumentation. The use of three capillaries having different inner diameters allows triplicate determinations of MMP from each experiment. Since the actual MMP pressure need not be reached during the experiment, MMP values that exceed the pressure ratings of the equipment can be reasonably estimated (e.g., MMPs using pure nitrogen). The method was used to determine the MMP pressure for crude oil samples from a conventional Muddy Formation reservoir in the Powder River Basin (API 35.8) and an unconventional Bakken Formation reservoir in the Williston Basin (API 38.7). The method is reproducible (typically < 4% RSD), and the method gave good agreement for a "live" Bakken oil with the results from a commercial laboratory's slim tube test. Approximately 80 MMP values were measured using pure CO_2, methane, and ethane, as well as 0-100% mole ratios of methane/CO_2, and methane/ethane. For both oil samples, ethane MMPs were ca. one-half those with CO_2, while methane MMPs were ca. double or triple those with CO_2. MMPs with mixed methane/CO_2 showed a linear increase with mole % methane for both crude oils while both oils showed an exponential increase in MMP with mole % methane in ethane, with little increase in MMP until ca. 20 mole % methane in ethane.

1. INTRODUCTION

Minimum miscibility pressure (MMP) is considered to be the pressure at which an injected fluid (CO_2, hydrocarbon gases, etc.) obtains "multiple contact miscibility" with reservoir oil at reservoir temperatures, and is a critical component for the design of miscible displacement enhanced oil recovery (EOR) processes in conventional reservoirs.[1] The "slim tube" test has been the industry standard to determine MMP for decades, but has received criticism from many investigators for being slow, expensive, having no consistent and widely-accepted operating parameters, and lacking a fundamental physiochemical definition of MMP.[2-9] The rising bubble method has also been used for rapid estimates of MMP, but is subject to operator interpretation since the MMP is determined by visual operation.[2,5,10-12] In contrast, the more recent, "vanishing interfacial tension" (VIT) test is more rapid (less expensive) than the slim tube test, and has a rigid definition of “miscibility,” i.e., MMP is the pressure at which the interfacial tension between two phases approaches zero.[3,5,13,14] Although some investigators have criticized the method since it does not mimic all of the interactions of flow and phase interactions that occur in a slim tube,[15-16] more recent work using measured IFT values (rather than calculated VIT estimates of miscibility as in refs. 15 and 16) showed good agreement with those determined using the slim tube test.[5] Two approaches can be used to measure IFT including the “pendant drop” and “capillary-rise” methods.[5, 14, 17-22] While the equations to determine IFT with both methods are well defined, the pendant drop is difficult to use at low IFTs between the two fluids, and thus the capillary-rise method is preferred to determine at which pressure the IFT approaches zero (i.e., MMP).[5]

The capillary-rise/VIT approach to determine MMP requires measuring the IFT between the bulk oil and the injected test fluid at each of several different pressures.[5] Determining the IFT at each pressure (at reservoir temperature) requires measuring the density of both upper and lower phases at each injection pressure, measuring the contact angle (θ) of the meniscus that occurs at the top of the oil column in the capillary tube at each pressure, and having an accurate measurement of capillary tube inner diameter.[5] However, simple manipulation of the equation for calculating IFT from these values and the height of the oil column shows that, if one is not concerned with actual IFT values at each pressure, ***but is only concerned with determining when IFT goes to zero***, then a simple extrapolation of the oil height vs. pressure yields a linear plot that intercepts the pressure axis at the MMP.[23,24] Thus, the need for determining fluid densities, contact angle, and an exact capillary inner diameter vanish, which substantially reduces the cost of the instrumentation and time required to measure MMPs.

2. EXPERIMENTAL SECTION

2.1. MMP Apparatus and Procedures. The apparatus used for the MMP determinations and detailed descriptions are shown in Figure 1. MMP determinations are performed with the following steps:

1. The capillaries and their rack are mounted into the cell by removing the window.

2. The cell is closed and swept several times with the test fluid.

3. A. For "dead" oil samples (Table I), the test oil is injected into the cell using a calibrated syringe, and the cell is immediately re-attached to the fluid inlet line. The volume of the injected oil is such that the top of the oil layer floods the capillary rack but leaves most of the capillaries' length exposed as shown in Figure 2 (left photo). The oil volumes can be varied by either plugging the cell's bottom ½-inch NPT port, or by attaching various lengths of capped ½-inch stainless steel pipe as an oil reservoir. Unless otherwise noted, the bottom port was plugged, resulting in a 3-mL oil volume flooding the capillary rack to the desired level as shown in Figure 2.

3. B. For "live" oil samples, the reconstituted oil sample is transferred to a 1-liter high-pressure vessel with water supplied by an ISCO 260D pump so that the entire oil/gas sample is transferred from the shipping vessel into the high-pressure vessel. The vessel is then heated in an air-circulating oven to reservoir temperature, pressurized to reservoir pressure with water, and rocked back and forth on a "teeter-totter" so that the water thoroughly mixes the components of the live oil sample. After at least one hour, the live oil sample is transferred slowly through a fluid-control valve into the cell

through a 1/16-inch stainless steel tubing fitting that was tapped into the ½-inch plug at the bottom of the cell. As soon as the crude oil floods the capillary stage as shown in Figure 2B, the fill valve is shut, and all other procedures are the same as for the "dead" oil samples.

4. The view cell (which now contains the oil sample and a headspace of the test injectant fluid at ambient pressure) is heated for one hour to the test temperature. (This heating time was verified to reach the test temperatures of 42 °C and 110 °C by monitoring the internal temperature with a thermocouple placed in the view cell interior.) The pressure in the cell is then recorded, and the video monitoring is begun.

5. Finally, the injectant test fluid pressure in the cell is increased by ca. 0.3 to 0.7 MPa (40 to 100 psi) increments in pressure by briefly opening the valve (C2). (Note, the pressure in the ISCO pump is typically held at the upper limit of the view cell, and the view cell pressure increased step-wise via the valve (C2). Valve (C2) is not left open after the brief fluid injection to eliminate back-flow of the CO_2/hydrocarbon mixture.) After allowing a suitable time for the fluids to equilibrate, the cell pressure is recorded along with a time signature to correspond to the video recording that occurs throughout the procedure.

6. The recorded video of the oil heights in the three capillaries at each test pressure is then displayed on a computer screen, and the height from the top of the bulk oil phase to the oil/CO_2 meniscus in each capillary tube is recorded by counting video pixels, yielding a capillary height resolution of <0.1 mm.

2.2. Preparing Mixed Fluids. Mixtures of methane in CO_2 and methane in ethane were prepared using two ISCO model 260D pumps. First, methane was transferred to a pump which was heated via a circulating water jacket and thermostatted bath at 45 °C to ensure that any mixture of methane in CO_2 or methane in ethane was single phase (i.e., above the supercritical temperatures for all of the test mixtures). The pump was then pressurized to 3000 psi and left to equilibrate for several hours. At the same time, a room temperature pump was filled with CO_2 (or ethane), pressurized to 3200 psi, and left to equilibrate for several hours. The moles of methane in the first pump were calculated based on pump volume and methane density and the volume of CO_2 (or ethane) needed to obtain the desired mole ratio was determined based on its density in the room-temperature pump. All fluid densities were obtained using the U.S. National Institute of Standards and Technology (NIST) software.[25]

After the fluids were mixed, the heated pump was left to equilibrate for one hour before collecting a gas bag for analysis, followed by periodic gas bag collections over one week to determine the mixture stability. Fortunately, this procedure resulted in stable mixtures. For example, the largest variation in a methane/CO_2 mixture over the one-week period was 41.6 to 42.9 mole % methane. However, to ensure that the composition of each gas mixture was accurately known, gas bag samples were collected for analysis immediately before and after each of the ca. 70 mixed fluid MMP determinations described below. (It should be noted that our initial procedure included cycling the pump from 3000 to 6000 psi in an attempt to better mix the two fluids, but this was found by gas bag analysis to yield mixtures that took up to 48 hours to stabilize, so the procedure was abandoned.)

3. RESULTS AND DISCUSSION

The changes in capillary height that occur with successive pressure increases with the injected fluid are shown in Figure 2 at the beginning of the injected fluid pressurization steps (left), at a pressure approximately one-half of the MMP (middle), and as the pressure approaches the MMP (right). Typical plots of the measured capillary heights for the three different diameter capillaries are shown in Figure 3. Depending upon the size of the pressure steps and the MMP for a particular system, the plot for each capillary contains ca. 10 to 25 measured data points, in contrast to the 5 or 6 data points typically determined in slim tube determinations of MMP.[9, 27] In addition, the use of the three capillaries in each experiment yields three measurements of MMP, thus reducing the chances of sporadic measurement errors influencing the final MMP value.

3.1. Method Optimization. In order to optimize the method, the effects of injected fluid/oil contact time, injected fluid/oil ratio, and the use of CO_2 with helium headspace pressure (to assist in filling the pump) were investigated.

Supply cylinders for CO_2 are often equipped with a dip tube and an overpressure of helium headspace to aid in filling CO_2 pumps. The dip tube is used to transfer liquid CO_2 to the pump (rather than the gas phase CO_2 at the top of the cylinder), and the helium overpressure helps to more efficiently transfer CO_2 to the pump. Although the presence of helium is generally thought not to affect CO_2 properties, we observed a significant rise in MMP determined at 42 °C when the effect of helium headspace was determined using the Muddy crude oil. For example, the MMP rose from ca. 9.7 MPa (1400 psi) with no helium present to ca. 10.3 MPa (1500 psi) with a 6.7 MPa (1000 psi) helium headspace in the CO_2 cylinder to ca. 15.9 MPa (2300 psi) when the pump was filled from a CO_2 cylinder with a ca. 9.7 MPa (1400 psi) headspace. Therefore, all subsequent studies were performed using CO_2 cylinders with no helium added (but with the dip tube). This lead to less efficient filling of the ISCO pump, but each MMP determination only uses ca. 15-25 mL of liquid CO_2 in the pump, so the inefficient pump fills are not a significant problem.

The second experimental variable optimized was the equilibrium contact time required between the injected fluid and the crude oil for each pressure increase. Although fluid/oil equilibrium must be achieved at each pressure step, shorter contact times are desirable both to reduce the time needed for each determination, as well as to allow smaller pressure increases thus giving more experimental data points for the MMP plots as shown in Figure 3. Ayirala and Rao[5] previously reported that one hour was sufficient to come to equilibrium, so we investigated the effect of contact time by performing five separate MMP determinations per oil using five different contact times between each pressure step of 1 minute, 2 minutes, 5 minutes, 30 minutes, and 60 minutes. Fortunately, there was no significant difference for either the Muddy oil's MMPs (at 42 °C) or the Bakken oil's MMPs (110 °C) between the values determined using any of the five different exposure times from 1 to 60 minutes. That is, the MMPs determined for each oil at all exposure times were well within one standard deviation unit of each individual MMP test as based on the results from the three capillaries (RSDs ranged from 0.1 to 3%). Therefore, subsequent MMP tests were done with one- or two-minute equilibrium times at each pressure step.

The third experimental variable investigated was the effect on measured MMP of the injected fluid/crude oil ratio, which was determined by comparing MMPs with 3 mL of the Muddy crude oil (using the view cell shown in Figure 1 with a plug in the bottom port) and 16.5 mL (using an identical view cell with a 4-inch long X ½-inch stainless steel capped pipe nipple replacing the ½-inch plug). The MMP determined using 16.5 mL of the Muddy crude oil was 9.67 ± 0.10 MPa (1.0% RSD), which is in excellent agreement with the triplicate values determined using 3 mL of oil given in Table 2. These results are consistent with those reported by Ayirala and Rao[5], where they found that varying the fluid/oil ratio from 20/80 to 80/20 mole % had no measurable effect on capillary height (and therefore MMP values determined by our method). These results also demonstrate that, as previously reported by Ayirala and Rao[5] the requirements for "multiple contact miscibility" are satisfied by the method, since changing the fluid/oil ratio had no measurable effect on the measured MMP values, nor did changing the exposure time at each new pressure. It should also be noted that the 16.5 mL oil volume greatly increased the height of the oil pool from oil swelling, which resulted in obscuring the bottom portions of the capillaries, thus substantially reducing the number of height measurements that could be obtained (and therefore reducing the data quality) as compared to using 3 mL of oil. Therefore, all subsequent experiments used 3 mL of oil for each MMP determination.

3.2. Method Robustness. MMPs for the two crude oils with pure CO_2, methane, and ethane are given in Table 2. The relative standard deviations presented are based on the MMPs from each of the three capillaries and are typically 5% or less. However, the reproducibility of replicate experiments (i.e., a fresh load of crude oil and a new set of capillary tubes) were significantly better, with the MMPs from triplicate experiments with the Muddy crude oil with CO_2 (42 °C) having an RSD of 0.5%, and the three experiments with Bakken crude oil with CO_2 (110 °C) having an RSD of 1.1%. Even in the worst two cases (Bakken with ethane at 110 °C and Bakken with methane at 42 °C) the duplicate experiments yielded MMPs that only varied by 2% (Table 2).

The long-term stability of the capillary-rise/VIT method was also tested by repeating MMP experiments with both crude oils three times over a 10-month period. As shown in Table 2, neither the Muddy oil (42 °C), nor the Bakken oil (110 °C), showed significant changes in the measured MMPs over ca. 10 months.

3.3. MMP Values with Pure and Mixed CO_2, Methane, and Ethane. Previous investigators have reported that the presence of methane in injected fluids increases MMPs, while ethane reduces MMPs,[10, 26-29] but experimental data points measured in a consistent manner using a single method (e.g., slim tube, rising bubble, or VIT) are few. Table 2 shows the large changes in MMP values obtained with CO_2, methane, and ethane under otherwise identical conditions. For both crude oils at 42 °C, MMPs are 3-fold higher using methane as compared to CO_2, while ethane reduces the MMPs to one-half those obtained with CO_2. For the Bakken crude at its reservoir temperature of 110 °C, methane doubles the MMP compared to CO_2, while, once again, ethane cuts the MMP by one-half. The low MMP values with ethane may be of particular interest for some reservoirs because of excess ethane resulting from producing pipe-line grade natural gas from shale plays. In some cases (e.g., the Bakken oil play in North Dakota), the cost of shipping ethane to an end user is likely to exceed its delivered value, making re-injection of ethane for EOR potentially attractive.

Table 2 also shows the profound effect reservoir temperature has on determining MMP. Although the effect of higher temperatures on raising MMP is known[9] it is often not recognized. For example, Bakken crude oil is considered to have a high MMP considering it is a fairly light (API 38.7) oil. However, as shown in Table 2, lowering the temperature from 110 °C to 42 °C reduces the MMP by one-half for both CO_2 and ethane. In contrast, there is only a slight drop in the methane MMP at 42 °C versus 110 °C. These results support those from earlier investigators that reservoir temperature can be more important than oil characteristics in determining MMP.[9] What is found in common for MMPs at the two temperatures is that the densities (of the pure fluids) at MMP are remarkably similar. So, for example, the MMP density of CO_2 for Bakken crude is 0.37 g/mL at both 110 °C (MMP = 17.4 MPa) and at 42 °C (MMP = 8.8 MPa).[25] The similarities in Bakken oil MMP densities for ethane (0.130 and 0.100 g/mL for 110 °C and 42 °C) and methane (0.154 and 0.183 for 110 °C and 42 °C) also show the importance of fluid density in determining MMP at different temperatures.

MMP values determined with the capillary-rise/VIT method for mixed fluids are given in Table 3 (Muddy crude oil) and Table 4 (Bakken crude oil). Similar to the pure fluid results in Table 2, reproducibilites of the three capillaries in each experiment are typically <5% RSD, while the MMPs from replicate experiments for each condition typically agree within 2%, showing good reproducibility of the method for mixed as well as pure fluids.

Interestingly, for both crude oils a simple linear regression fits the mixed methane/CO_2 MMP results well, showing that the effect of methane in raising CO_2 MMPs is linearly related to its mole fraction (Figures 4 and 5). In contrast, MMP values for both crude oils show exponential behavior for the methane/CO_2 mixtures. Therefore, the effect of methane content in CO_2 (as in recycle operations) increases the MMP more rapidly at lower concentrations than does methane in ethane. The MMPs for the mixed methane/ethane also indicate that the purity of ethane intended for EOR need not be very high since there is little effect on MMP until methane reaches 15-20 mole % in ethane, and other investigators have shown that the presence of other natural gas liquids (propane, butane, etc.) will only enhance the ability of ethane to achieve MMP.[14, 26-29]

3.4. MMP Determinations with "Live" Oil and Comparison to Slim Tube. Two live oil samples from the Bakken were supplied by a Bakken producer and reconstituted to reservoir compositions as described above. A replicate sample was retained by the contract PVT lab that prepared both live oil samples. MMP values using the capillary-rise/VIT method were measured and reported to the producer without prior knowledge of the slim tube results provided by the contract PVT lab. MMP determinations for each sample were performed in five replicate experiments, each with three different diameter capillaries as before.

The mean MMP for the five capillary-rise/VIT determinations of crude oil A (129 °C) was 21.92 ± 0.79 MPa (3.6% RSD) which was in good agreement with the slim tube value reported by the PVT lab of 21.79 MPa, and the equation of state value reported by the producer of 22.20 MPa. Although the slim tube MMP was not available for the live crude oil B (126 °C), the measured value using capillary-rise/VIT was 22.04 ± 0.99 MPa (4.5% RSD), which is in reasonable agreement with the producer's equation of state value of 21.72 MPa. (RSDs for the three capillaries in each individual experiment were ≤5% as they were for the dead oils.) These results and Ayirala and Rao's earlier reports showing good agreement between capillary-rise/VIT and slim tube support the use of this technique instead of (or in conjunction with) the slim tube method.

As would be expected, measuring the MMPs of live oils is more difficult than with "dead" oils described above. Heating, mixing, and pressurizing the live oil samples supplied by the contract PVT lab is not difficult, nor is transferring the live oil into the MMP view cell. The difficulty with live oils occurs because of the requirement of the method to begin at near-ambient pressure. Though the live oil is transferred efficiently to the view cell, the low pressure (and high temperatures for these Bakken crude oils) causes degassing which can result in gas bubbles in the capillaries, making them useless until the bubbles re-dissolve or migrate out of the capillaries during the subsequent pressurization steps. This usually occurs during the first few pressure steps, but sometimes the bubbles make obtaining oil height data impossible for that particular experiment. For example, useful height data was obtained for all three capillaries for four of the five experimental runs for oil sample B, but no data was possible to obtain from one of the experiments because of bubbles in all three capillary tubes. Similarly, only one of the five experimental runs for oil sample A yielded height data for all three capillaries, but useful height data was obtained from two of the capillaries in the other four experiments, which still yields duplicate MMP values from each experiment. Also note that, since two MMP experiments can be performed with the same live oil per day, the occasional failure to obtain useable data because of bubbles in the capillaries is acceptable.

3.5. Very High Pressure MMPs. An additional advantage of the capillary-rise/VIT technique is that the pressure does not have to reach MMP to estimate MMP since the pressure versus capillary height line is extrapolated to the MMP value. Therefore, MMP values can reasonably be estimated for fluids with very high MMPs without the need for the equipment capable of reaching those pressures. This is demonstrated in Figure 6 for the MMP of Bakken crude oil with pure nitrogen at 42 °C. Capillary heights were obtained from ambient pressure to 34.5 MPa (5000 psi) which was the upper limit of the pressure gauge used for the determinations. (Note that no data was available from the smallest capillary, because of the high surface tension of the nitrogen/oil system.) Based on linear extrapolation to zero oil height, the MMP of Bakken crude oil at 42 °C (Figure 6) was 154.2 ± 5.8 MPa (22370 ± 840 psi), while at 110 °C, the MMP was 101.4 ± 1.1 MPa (14710 ± 160 psi). In contrast to CO_2 where higher temperatures cause substantially higher MMPs, the higher temperature with the Bakken crude oil showed a moderate decrease in MMP, possibly indicating the importance of vaporization of the crude oil components to lower the surface tension with nitrogen. Although the MMPs determined by extrapolating to such high MMP values are certainly not as accurate as being able to cover the full pressure range from ambient to MMP, these results do show that MMPs can at least be estimated for systems that far exceed pressure limits of the experimental apparatus.

4. CONCLUSIONS

Simple modifications to Ayirala and Rao's capillary-rise/VIT method reported here greatly decrease the apparatus cost and complexity by eliminating the need to measure both fluid densities and contact angle at each test pressure, as well as the need for capillaries with accurately-known internal diameters. The simple, yet thermodynamically-rigid definition of MMP as the pressure where the interfacial tension between two fluid phases goes to zero makes the capillary-rise/VIT method less susceptible to operational differences and operator interpretations among different labs that affect methods such as the rising bubble and slim tube techniques. MMP values above the pressure limits of the apparatus can be estimated, since the method does not require pressures at or above MMP. The method presented here is reproducible, only requires 3 mL of crude oil per determination, and can be performed with live oil (two determinations per day) or dead oil (three or four determinations per day) with one experimental apparatus. The previous reports showing good agreement between the slim tube and the capillary-rise/VIT method, as well as the good agreement obtained in the present study for a live oil, support the use of capillary-rise/VIT as a supplement to, and/or replacement for, the slim tube method. The efficiency of the method allows the effects on MMP of a large number of variables such as different potential injectant fluids (and their mixtures), changing fluid composition during recycle operations, temperature, and crude oil composition to be cost-effectively measured as evidenced by the ca. 80 experimental MMP values reported here.

FIGURES

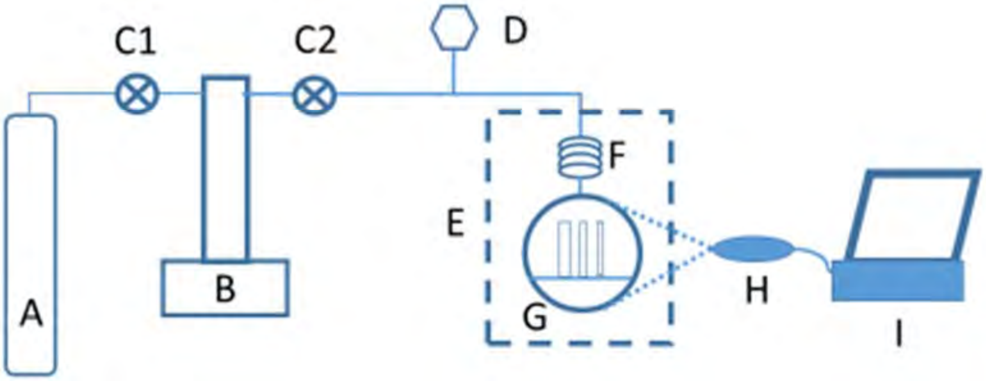

Figure 1. Experimental apparatus for measuring MMP using capillary-rise/VIT. The components area (A) CO_2 supply cylinder with dip tube, (B) an ISCO Model 260D syringe pump (ISCO-Teledyne, Lincoln, Nebraska, USA), (C) fluid control/shut-off valves, (D) digital pressure gauge calibrated to a dead weight tester, (E) an Agilent Model 5890 gas chromatographic oven with the door modified to include a 1.3-cm thick polycarbonate view port (the oven provides fan-circulated heat within 0.1 °C of the set-point), (F) a 1/16 inch stainless steel pre-heating coil, (G) a high pressure view cell (Inferno Manufacturing Corporation, Shreveport, Louisiana, USA), model SFI 111 for pressures up to 20.7 MPa (3000 psi), and model SFI 6000 for pressures up to 41.4 MPa (6000 psi). The cell contains a 1.0-cm-wide X 3.0-cm-long home-made stainless steel rack holding three ca. 15 mm-long glass capillary tubes with their bottoms suspended in a pool of oil. The capillary tubes have inner diameters of (left to right) 1.12, 0.84, and 0.68 mm, respectively (World Precision Instruments, Inc., Sarasota, Florida, USA). The oil heights are monitored with a video camera (H) and recorded on a computer (I).

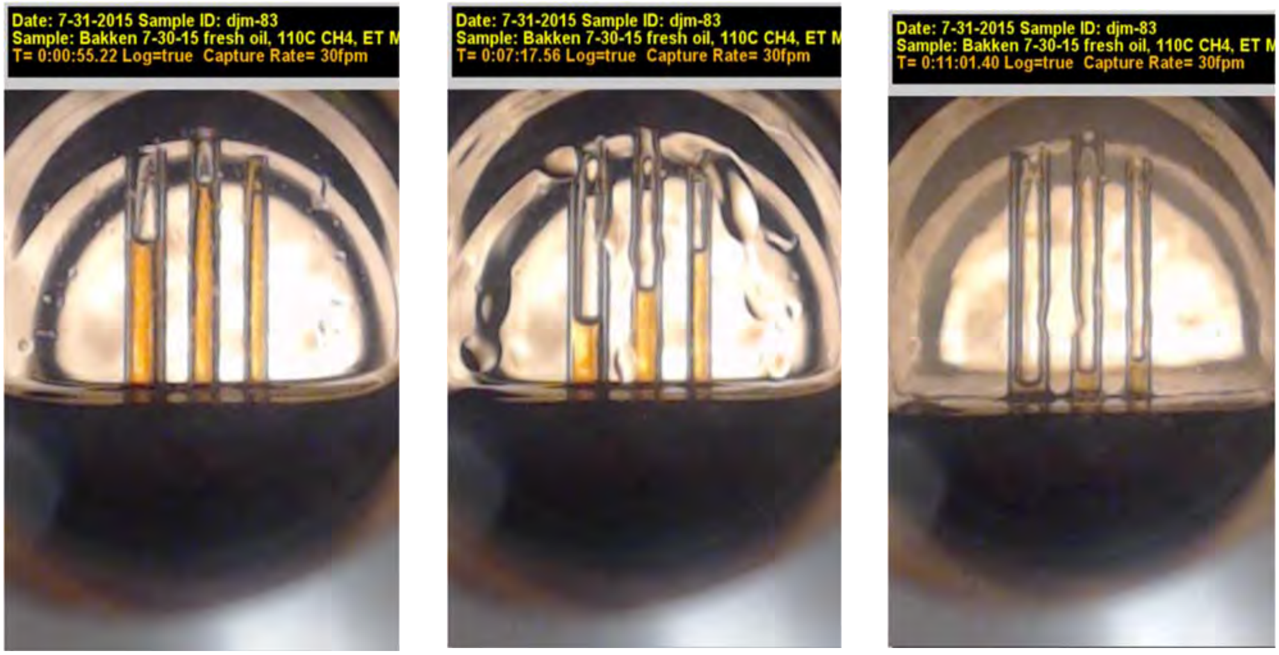

Figure 2. Photos of the oil height in three capillaries (1.12-, 0.84-, and 0.68-mm inner diameters from left to right in all photos) at low pressure (left photo), the pressure ca. ½ of MMP (middle), and as the pressure approaches MMP (right photo).

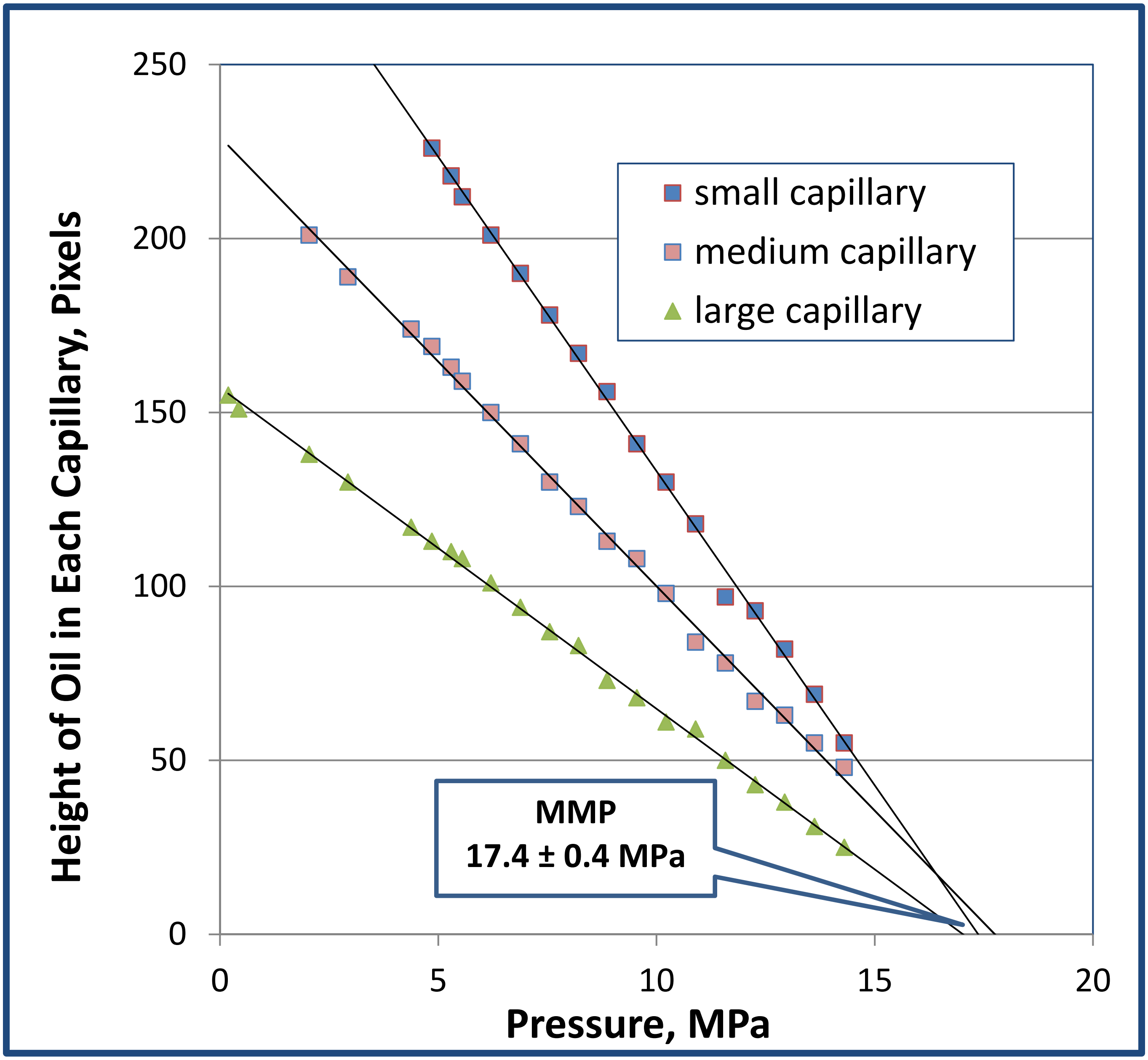

Figure 3. Capillary-rise/VIT plot for the measuring MMP of Bakken crude oil at 110 °C with pure CO_2.

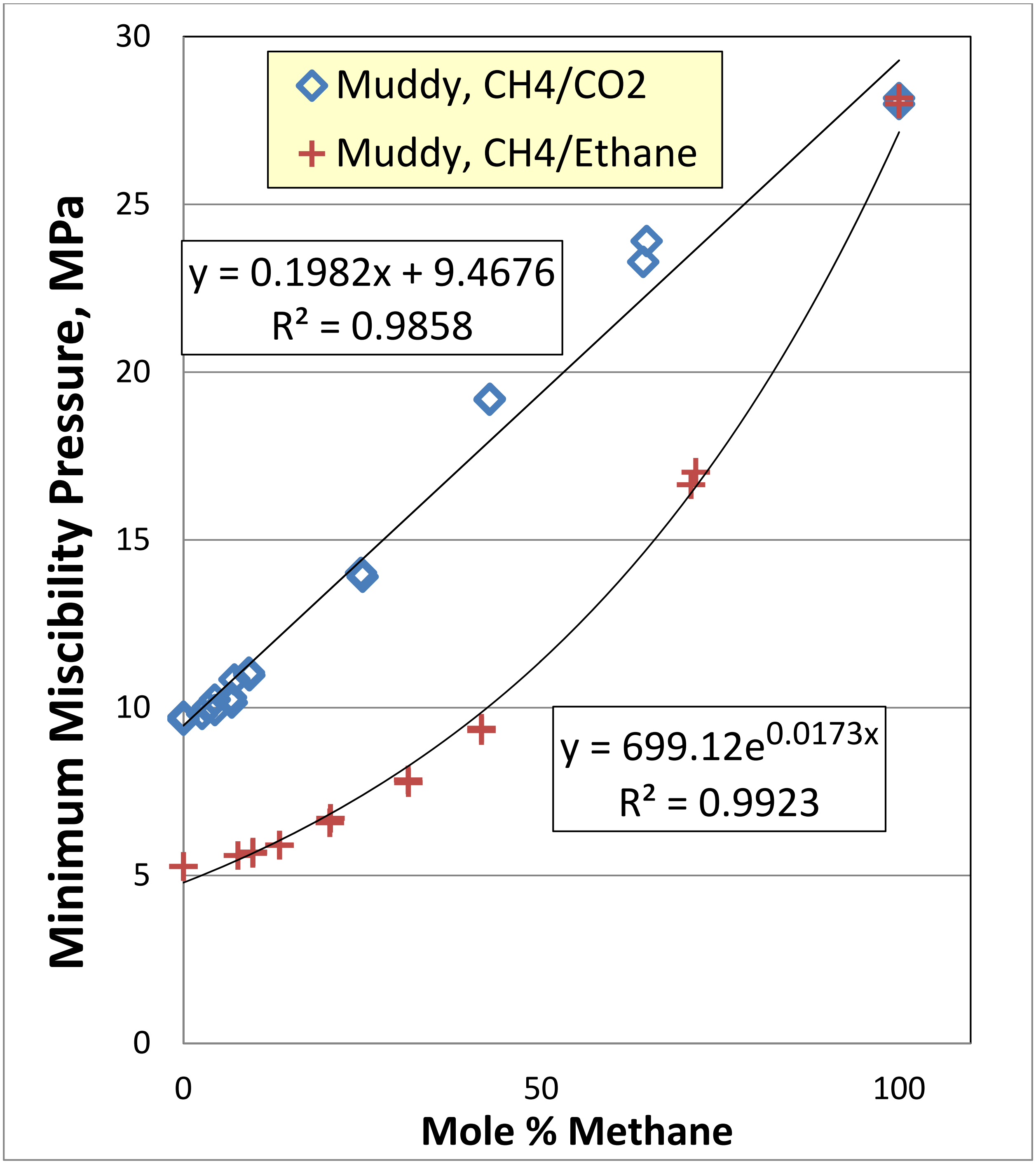

Figure 4. Effect of different concentrations of methane in CO_2 and in ethane on measured MMP values for the Muddy crude oil at 42 °C.

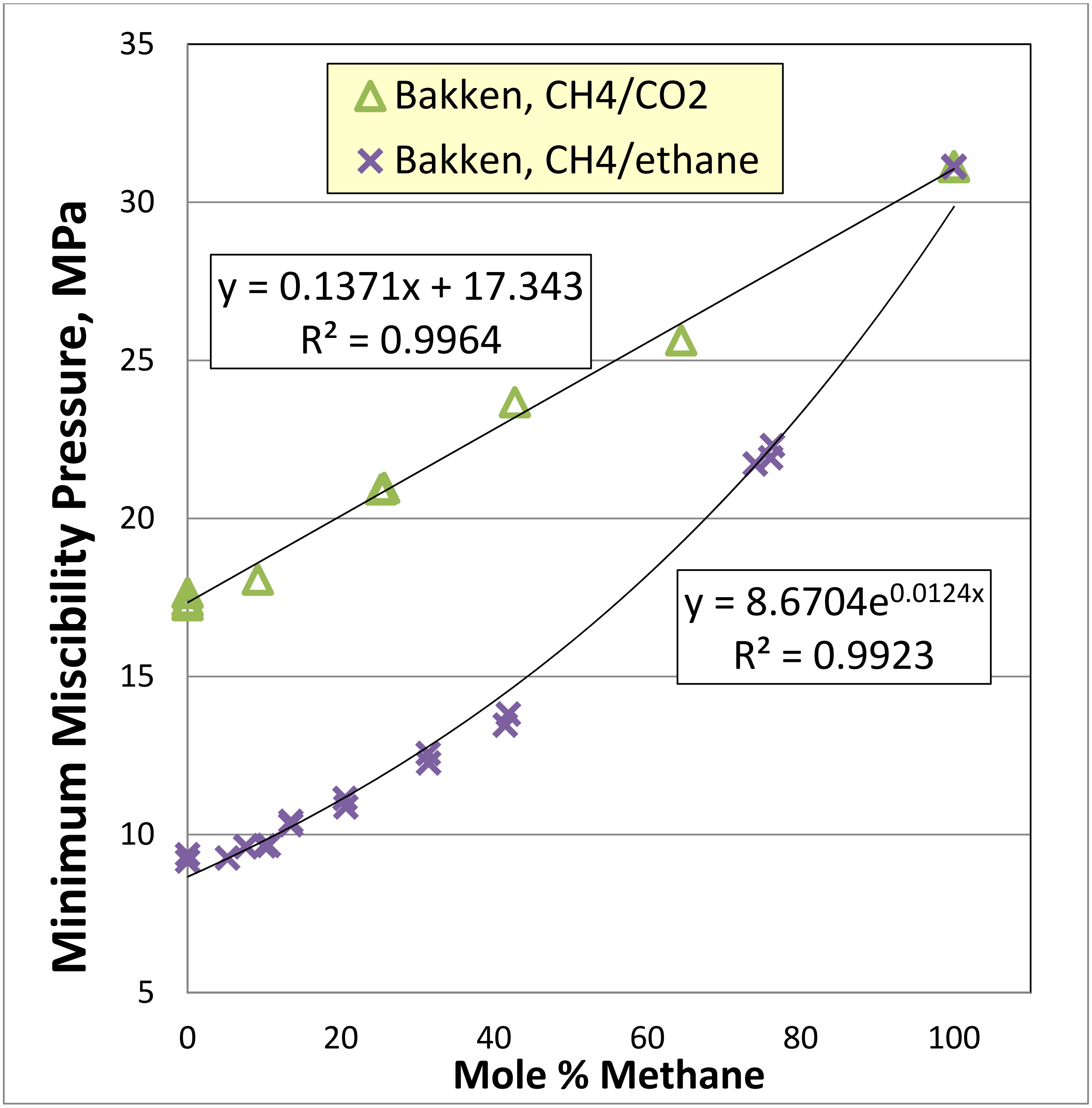

Figure 5. Effect of different concentrations of methane in CO_2 and in ethane on measured MMP values for Bakken crude oil at 110 °C.

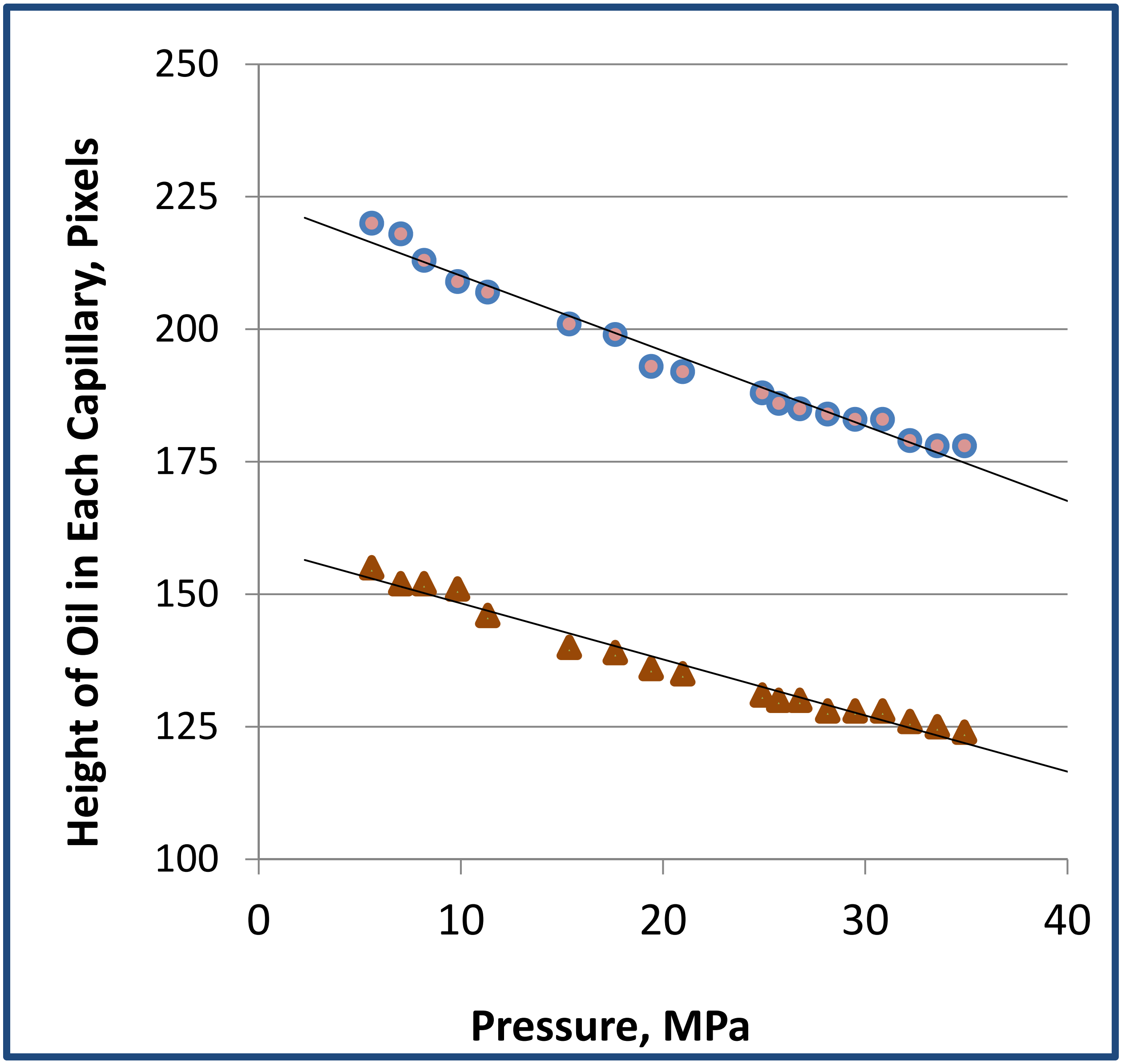

Figure 6. Estimating MMP using nitrogen for the Bakken crude oil at 42 °C. MMPs were estimated by linear extrapolation of the oil height data from the 34.5 MPa (5000 psi) upper pressure limit of the system pressure gauge to zero height, which occurred at a mean MMP of 154.2 ± 5.8 MPa. Data was available only for the medium and large-diameter capillaries, because of the very high initial surface tension of the nitrogen/crude oil system.

Table 1. Crude oil characterisation.

		Muddy	**Bakken**
Initial Reservoir Conditions			
Reservoir Pressure	MPa	8.27	55.16
Reservoir Temperature	°C	42	110
Saturation Pressure	MPa	6.38	17.44
Compressibility @ Reservoir Pressure	Pa^{-1}	1.11E-09	1.15E-09
Compressibility @ Saturation Pressure	Pa^{-1}	1.40E-09	2.93E-09
At Saturation Pressure and Reservoir Temperature			
Oil Formation Volume Factor	m^3/Sm^3	1.10	1.71
Solution Gas-Oil Ratio	Sm^3/Sm^3	30.9	162.9
Oil Density	g/mL	0.79	0.65
Oil Viscosity	Pa-s	2.22E-03	3.92E-04
At Ambient Pressure and Reservoir Temperature			
Residual Oil Density	g/mL	0.82	0.79
Residual Oil Viscosity	Pa-s (N-s/m^2)	0.00365	0.00134
At Stock Tank Conditions			
Residual Oil Density	g/mL	0.85	0.83
API Gravity		35.8	38.7
Oil Type		Black Oil	Black Oil

	Muddy		**Bakken**	
Oil Composition	**Original**	**Residual**	**Original**	**Residual**
Component	Mole frac.	Mole frac.	Mole frac.	Mole frac.
CO_2	0.0042	0	0.0032	0
N_2	0.0019	0	0.0322	0
CH_4	0.1909	0	0.2687	0
C_2H_6	0.0033	0.0009	0.1080	0
C3H to NC4	0.0428	0.0370	0.1309	0.0001
IC5 to C07	0.1526	0.1881	0.1369	0.0884
C08 to C13	0.2860	0.3606	0.1840	0.4770
C14 to C24	0.1997	0.2523	0.0947	0.3016
C25 to C36+	0.1184	0.1612	0.0415	0.1329
C7+%	60.41	77.41	32.02	91.15

Table 2. MMPs for the Muddy and Bakken crude oils with pure CO_2, methane, and ethane.

Crude Oil	Fluid	Temp. (°C)	density, g/mL[a]	MMP, MPa[b]	SD	% RSD
Muddy	CO_2	42	0.542	9.67	0.30	3.1
				9.73	0.29	3.0
				9.65	0.47	4.9
Muddy	methane	42	0.187	27.99	1.53	5.5
				28.17	0.30	1.1
Muddy	ethane	42	0.122	5.27	0.10	1.8
				5.27	0.12	2.3
Bakken	CO_2	110	0.37	17.38	0.37	2.1
				17.64	0.15	0.8
				17.26	0.14	0.8
Bakken	methane	110	0.154	31.11	1.17	3.7
				31.14	1.72	5.5
Bakken	ethane	110	0.130	9.37	0.32	3.5
				9.17	0.35	3.8
Bakken	CO_2	42	0.366	8.86	0.26	2.9
				8.77	0.16	1.8
Bakken	methane	42	0.183	27.44	1.28	4.7
				26.83	1.36	5.1
Bakken	ethane	42	0.100	4.91	0.08	1.7
				4.90	0.08	1.5

[a] Average fluid densities for the replicate MMP values are listed for the pure fluids at the stated pressures and temperatures.

[b] Mean MMPs and standard deviations are based on the MMP values from each of the three capillary tubes used for each determination.

Table 3. MMPs determined with capillary-rise/VIT for the Muddy crude oil (42 °C) with mixed methane/CO_2 and methane/ethane.

Mole % methane in CO_2	MMP[a] (Mpa)	SD[a]	% RSD[a]
0	9.67	0.30	3.1
0	9.73	0.29	3.0
0	9.65	0.47	4.9
2.6	9.82	0.06	0.6
3.4	10.01	0.24	2.4
4.4	10.24	0.60	5.8
4.4	9.93	0.17	1.7
6.6	10.31	0.16	1.6
6.7	10.15	0.24	2.4
7.1	10.84	0.26	2.4
9.2	11.05	0.10	0.9
9.2	10.97	0.03	0.3
24.8	14.02	0.55	3.9
25.0	13.90	0.78	5.6
42.8	19.18	0.68	3.5
42.8	19.21	0.24	1.3
64.3	23.29	0.76	3.3
64.7	23.91	1.20	5.0
100	27.99	1.53	5.5
100	28.17	0.30	1.1

Mole % methane in ethane	MMP[a] (Mpa)	SD[a]	% RSD[a]
0[b]	5.27	0.10	1.8
0[b]	5.27	0.12	2.3
7.6	5.59	0.07	1.2
9.7	5.66	0.09	1.6
9.7	5.70	0.11	2.0
13.4	5.91	0.11	1.9
13.4	5.90	0.14	2.4
20.5	6.57	0.22	3.4
20.6	6.70	0.10	1.5
31.4	7.85	0.14	1.7
31.5	7.77	0.23	2.9
41.7	9.39	0.37	4.0
41.7	9.32	0.28	3.0
70.9	16.64	0.79	4.7
71.6	17.02	0.30	1.8
100[c]	27.99	1.53	5.5
100[c]	28.17	0.30	1.1

[a] MMP, standard deviation, and RSD values are based on the three capillaries used in each experimental run.

Table 4. MMPs determined with capillary-rise/VIT for the Bakken crude oil (110 °C) with mixed methane/CO_2 and methane/ethane.

Mole % methane in CO_2	MMP[a] (Mpa)	SD[a]	% RSD[a]
0.0	17.38	0.37	2.1
0.0	17.64	0.15	0.8
0.0	17.26	0.14	0.8
9.2	18.06	0.65	3.6
25.3	20.92	0.53	2.5
25.7	20.96	0.43	2.0
42.7	23.67	1.27	5.4
64.4	25.63	0.82	3.2
100.0	31.11	1.17	3.7
100.0	31.14	1.72	5.5

Mole % methane in ethane	MMP[a] (Mpa)	SD[a]	% RSD[a]
0.0	9.37	0.32	3.5
0.0	9.17	0.35	3.8
5.2	9.26	0.29	3.1
7.6	9.62	0.16	1.6
7.6	9.63	0.18	1.8
10.0	9.65	0.31	3.3
10.5	9.66	0.37	3.8
13.5	10.31	0.36	3.5
13.5	10.42	0.34	3.3
20.5	11.14	0.24	2.1
20.6	10.88	0.39	3.6
31.4	12.57	0.54	4.3
31.5	12.27	0.35	2.9
41.5	13.47	0.62	4.6
41.9	13.82	0.52	3.8
74.1	21.73	0.80	3.7
76.1	21.92	0.22	1.0
76.3	22.30	0.98	4.4
100	31.11	1.17	3.7
100	31.14	1.72	5.5

[a] MMP, standard deviation, and RSD values are based on the three capillaries used in each experimental run.

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Notes

The authors declare no competing financial interest.

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APPENDIX B

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

Comparison of Soil-to-Water Suspension Ratios for Determining Electrical Conductivity of Oil-Production-Water Contaminated Soils

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Abbreviations: EC, Electrical conductivity; $EC_{1:1}$, 1:1 soil-to-water suspension EC; $EC_{1:5}$, 1:5 soil-to-water suspension EC; EC_e, saturated paste extracts EC; SAR, sodium adsorption ratio; RMSE, root mean square errors

Key words: Soil salinity, electrical conductivity, oil production, saturated paste, soil-to-water suspension, brine

Short Title: Soil-to-Water Suspension Ratios for Oil-Production-Water Contaminated Soils

ABSTRACT

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

INTRODUCTION

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

Soil contamination from oil and geothermal production brines, with similar solution chemistries as those in North Dakota, have been reported in Kansas (Latta, 1963), Ohio (Munn and Stewart 1989), Oklahoma (Atalay et al. 1999; Sublette et al. 2005; Sublette et al. 2007), Pennsylvania (Dresel and Rose 2010), Texas (McFarland et al. 1987), and California (Jury and Weeks 1978). Oil and geothermal production brine is a concentrated mixture of dissolved salts; the most abundant being sodium chloride (NaCl) (Aschenbach and Kindscher 2006). These brines can have an electrical conductivity (EC) up to four times greater than those observed in seawater (e.g., 200 dS m^{-1}) (Jury and Weeks 1978; Keiffer and Ungar 2002). As of August 20th, 2015, approximately 77 million liters of brine have been spilled on and off drill pads during the oil and gas exploration in western North Dakota since Feb. 9th, 2001 (Figure 1; data summarized from the North Dakota Department of Health spill database). During this time, 6,068 brine spills have been reported to the North Dakota Department of Health and the North Dakota Industrial Commission (ND DOH 2015). Once brine has been released onto the soil surface, the soil becomes sterile and void of vegetation, which can persist for decades until the salts are reduced or removed (Murphy 1988). Since the early 2000s, these spills have resulted in thousands of brine spill reclamation efforts that require effective and rapid site characterization tools.

Many soil EC methods have been assessed in an effort to improve efficiency and reduce costs for determining soil salinity. Determining the extent of salinity using various soil-to-water suspension ratios (e.g., 1:1, 1:2, 1:2.5, 1:5, and 1:10 soil-to-water suspensions) is a more time-and cost-effective method as compared to using the standard saturated paste extract EC_e (Sonmez et al. 2008; He et al. 2013). Remediation strategies for brine spills rely on having accurate, reliable, and timely data so that the spill area can be delineated and contained, and so first-response remediation actions can be made. Currently, most assessment strategies involve using saturated paste extracts, and can take over 48 hr to get results. Using soil-to-water suspensions with shorter equilibration and preparation times will drastically reduce the work and time involved in obtaining soil EC measurements. Soil testing laboratories and land-reclamation consultants in Australia and China commonly use the 1:5 soil-to-water suspensions as well as 1:1 soil-to-water suspensions in the United States and Canada (Hogg and Henry 1984; Rayment and Lyons 2011; Wang et al. 2011; He et al. 2013). Sonmez et al. (2008) observed high correlations between EC_e and the EC values of 1:1, 1:2.5, and 1:5 soil-to-water suspensions for soils in Turkey with a slightly better correlation using the 1:2.5 suspension.

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

(Hogg and Henry 1984; Ozcan et al. 2006; Sonmez et al. 2007; He et al. 2013). The development and validation of conversion equations in the range of EC_e observed in brine spill sites are lacking (Zhang et al. 2005; Chi and Wang, 2009).

One study successfully developed conversion equations for soils with EC_e ranging from 1 to 227 dS m^{-1} for sodium (Na^+) based soils (Chi and Wang 2010). However, their equations do not address an apparent heteroscedasticity as observed in another conversion equation study done on naturally-occurring saline soils by He et al. (2013). Another study on naturally-occurring saline soils observed a strong correlation ($r^2 = 0.98$) between $EC_{1:1}$ and EC_e for medium textured soils with an EC_e ranging from 0.2 to 42.1 dS m^{-1} (Hogg and Henry 1984). Sonmez et al. (2008) developed equations for converting $EC_{1:1}$, $EC_{1:2.5}$, and $EC_{1:5}$ to EC_e using sandy, loamy, and clayey soils with soil EC_e values ranging from 0.2 to 17.7 dS m^{-1}. The soils used by Sonmez et al. (2008) were treated with NaCl, KCl, and $CaCl_2$ solutions. However, conductivity factors are specific to ion species and associations (Tolgyessy 1993). Therefore, caution should be taken when using conversion equations if the general solution composition is not known.

The reported differences in conversion factors (i.e. the slope factor of a linear model to predict ECe from a soil-to-water suspension) of soil-to-water suspensions between 1:1 and 1:5 range from 3.84 to 5.56 (USDA 1954; Hogg and Henry 1984; Zhang et al. 2005; Ozcan et al. 2006; Sonmez et al. 2008). In comparison, soil texture contributes a minimal influence on conversion factors with reported differences among soil textures ranging from 0.05 to 0.86 (Hogg and Henry 1984; Sonmez et al. 2008).

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

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

MATERIALS AND METHODS

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

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

The 1:1 and 1:5 soil-to-water suspensions were made by adding together 10 g of soil and 10 mL of deionized (DI) water, and 5 g of soil and 25 mL of DI water, respectively. Then, the soil-to-water suspensions were equilibrated using a slightly modified procedure from He et al. (2015). Each 1:1 and 1:5 suspension was manually stirred for 10 s with a glass stir rod, and allowed to equilibrate for at least 18 h, which is greater than the 8 h recommendation by He et al. (2012). Longer equilibration times were used in this study to ensure complete NaCl dissolution. A subset of soil-to-water suspensions (n = 5) representing a large range of soil salinity were also analyzed for EC using 0, 0.17, 0.5, 2, 4, 8, and 18 hr equilibration times to determine if and when an equilibration would occur. Each soil-to-water suspension was stirred with a glass rod for another 10 s before measuring EC. The 1:1 and 1:5 soil-to-water suspension ($EC_{1:1}$ and $EC_{1:5}$, respectively) were then measured for EC using a Sension 378 conductivity probe (Hach Co., Loveland, CO, USA) which has an operating range of 0 to 199.9 dS m^{-1}.

Saturated Paste Extract (EC_e)

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

Equation Development and Validation

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

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

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

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

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

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

RESULTS

General Soil Properties and Soil EC Extract Relationships

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

Saturated paste extract Na^+ and SAR values ranged from 1 to 828 mmol L^{-1} and 0.3 to 72 SAR, respectively (Tables 2 and 3). Saturated paste extract Na was highly correlated with soil

EC_e, $EC_{1:1}$, and $EC_{1:5}$ values at coefficient of determination (r^2) values of 0.91, 0.86, and 0.86, respectively (Figure 3). In contrast, saturated paste extract Ca and Mg correlated poorly to all three soil EC methods with r^2 values ranging from 0.42 to 0.55 and 0.25 to 0.28, respectively (Figure 3).

The relationships among EC extract methods had r^2 values of 0.97, 0.97, and 0.91 for $EC_{1:1}$ vs. $EC_{1:5}$, EC_e vs. $EC_{1:1}$, and EC_e vs. $EC_{1:5}$, respectively, with RMSE's ranging from 0.06 to 0.10 (Figures 4 and 5). Based on these analyses, soil EC_e can be accurately estimated from a measured $EC_{1:1}$ and $EC_{1:5}$ value across a large range (i.e., 0 to 126 dS m^{-1}) using the following equations:

$$\mathbf{EC_{1:5} = 10^{0.9749\,(Log\,EC_{1:1})\,-\,0.3122}} \qquad (4)$$

$$\mathbf{EC_{1:1} = 10^{1.0257\,(Log\,EC_{1:5})\,+\,0.3202}} \qquad (5)$$

$$\mathbf{EC_{e} = 10^{1.2562\,(Log\,EC_{1:5})\,+\,0.7659}} \qquad (6)$$

$$\mathbf{EC_{e} = 10^{1.2533\,(Log\,EC_{1:1})\,+\,0.3533}} \qquad (7)$$

Validation of Equations

The above conversion equations were validated against an independent dataset of different soils from the three remaining sites not used in developing and calibrating the equations (Figures 4 and 5). Validation RMSE values ranged from 1.8 to 15 and 4.2 to 16 dS m^{-1} using $EC_{1:1}$ and $EC_{1:5}$ values, respectively. Overall RMSE for $EC_{1:1}$ and $EC_{1:5}$ values were 6.1 and 7.6 dS m^{-1}, respectively. Bias values were 2.57, 2.31 and -0.18 dS m^{-1} for $EC_{1:1}$ vs. EC_e, $EC_{1:5}$ vs. EC_e, and $EC_{1:1}$ vs. $EC_{1:5}$, respectively. RMSE and bias values became larger as measured EC_e increased. Estimates for converting to saturated paste (EC_e) values using a 1:1 soil-to-water ratio had the lowest RMSE values (Figure 4). This indicates that $EC_{1:1}$ estimates were closer to the measured data than the $EC_{1:5}$ estimates. During the validation, an underestimation of EC_e values tended to occur for soils with EC and SAR values greater than 85 dS m^{-1} and 60, respectively.

DISCUSSION

Similar to the results reported here, He et al. (2013) observed curvilinear trends while comparing soil EC methodologies. They developed a natural log transformed equation [$EC_e = e^{0.70(\ln EC_{1:5})+1.78}$] for converting between $EC_{1:5}$ and EC_e in Ca^{2+} and SO_4^{2-} based soils with naturally occurring salinity. In contrast, Chi and Wang (2010) observed good relationships ($r^2 = 0.94$) in Na^+ based soils of China, but did not consider issues of heteroscedasticity in their analysis.

Our newly developed equations were compared with 14 equations derived from nine other EC conversion studies (Figure 6). The same validation data set, as mentioned previously, was used for the comparisons. Among the equations developed here and the other 14 equations reported in the literature, our $EC_{1:1}$ and $EC_{1:5}$ conversion equations were the most accurate followed by the 1:5 soil-to-water ratio equation developed by Chi and Wang (2009) (r^2=0.94) at predicting EC_e on brine contaminated soils based on RMSE values. This was expected since Chi and Wang (2009) used soils with similar Na^+ content as the current study to develop their EC conversion equation. Therefore, their EC_e is also likely to be highly correlated with Na content as in the present study (Figure 3).

Although the Chi and Wang (2009) equation performed well at high and low EC_e values, the equation substantially overestimated EC_e values in the 5 to 35 dS m^{-1} range, whereas our equations did not. As mentioned previously, their overestimations are likely due to the lack of homoscedasticity during their analysis. Equations developed by Hogg and Henry (1984), Khorsandi and Yazdi (2011), and He et al. (2013) were the least accurate at predicting EC_e from $EC_{1:1}$ and $EC_{1:5}$ values, with RMSE of 27.4, 24.6, and 27.3 dS m^{-1}, respectively. In contrast, Chi and Wang (2009) and our new equations for predicting EC_e from $EC_{1:1}$ and $EC_{1:5}$ values were the most accurate, with RMSE of 7.63 and 6.13 to 7.62 dS m^{-1}, respectively (Table 4). With the exception of the Chi and Wang (2009) equation, all other equations produced RMSE of 2 to 4.5 times greater than those observed for the equations 6 and 7 presented in this study.

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

Researchers and land managers can make any of these soil-to-water suspensions with equal time and effort. The equal effort to make the suspensions and the high correlation of all soil-to-water suspension to EC_e demonstrate the arbitrary nature of each soil-to-water ratio. Although arbitrary, greater errors can occur in predicting EC_e as the difference between soil and water in suspensions increases if suspensions are prepared by increasingly smaller soil quantity.

In other words, if the soil sample used to create a suspension decreases below a representative soil sample, then repeatability of the results is sacrificed.

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

These new conversion equations will be applicable to soils contaminated with NaCl dominated brines as well as NaCl-based naturally-occurring soil salinity due to deep ground water seeps. Since these equations are valid for soil EC_e from 0.4 to 126 dS m^{-1}, they can be used for soils classified as both saline and non-saline. However, if brine contaminated soils contain significant quantities of other dissolved salts (e.g., Ca, Mg, and SO_4^{2-} based salts) and the EC is not well correlated with NaCl, then ion pairing can result in conductivity factors that differ from NaCl. In these cases, the new conversion equations may over-estimate EC_e and not be applicable for such soils (Figure 6; Table 4).

CONCLUSIONS

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

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

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FIGURE CAPTIONS LIST

Figure 1. Cumulative brine spilt on and off oil drill pads during and after oil and gas exploration efforts in North Dakota from February 9th 2001 through August 20th 2015 summarized from the North Dakota Department of Health spill database. The first date coincides with when the North Dakota spill records began reporting the amount of brine spilled.

Figure 2. Equilibration times for $EC_{1:1}$ and $EC_{1:5}$. Time periods ranged from 0 to 18 hr. Soil EC values did not differ with time ($P > 0.20$). Panels A and B are $EC_{1:1}$ and $EC_{1:5}$, respectively.

Figure 3. Saturated paste extract Na, Ca, and Mg levels (Panels A, B, and C, respectively) and their relationships to EC_e, $EC_{1:1}$, and $EC_{1:5}$.

Figure 4. Equation development and validation for EC_e vs. $EC_{1:1}$ and EC_e vs. $EC_{1:5}$. Panels A and B are the equation developments for EC_e vs. $EC_{1:1}$ and EC_e vs. $EC_{1:5}$, respectively. Panels C and D are the validations for $EC_{1:1}$ and $EC_{1:5}$ conversion equations, respectively.

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

Figure 6. Comparison of 14 developed EC_e conversion equations from nine previous soil salinity studies to those developed in this study. Measured values are from a set of 44 validation soil samples. Circles (gray and black) indicate EC_e predictions based on our newly developed $EC_{1:5}$ and $EC_{1:1}$ conversion equations.

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

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

[z]=Taxonomic descriptions for each series in complex

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

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

		Soil Chemical Property									
	Statistic	^{z}EC$_{1:1}$	EC$_{1:5}$	EC$_{e}$	^{y}TDS$_{1:1}$	TDS$_{1:5}$	TDS$_{e}$	SAR^{x}	Na^{+}	Ca^{2+}	Mg^{2+}
			------- dS m^{-1} -------			----------- g l^{-1} -----------			------- meq l^{-1} -------		
Site 1	Mean	4.02	2.15	13.3	2.57	1.37	8.49	4.47	38.7	44.7	76.6
	Median	3.25	1.94	8.42	2.08	1.24	5.39	3.15	21.4	36.3	33.0
	Minimum	1.48	0.77	3.66	0.94	0.49	2.34	0.32	2.02	24.7	8.56
	Maximum	9.66	4.53	35	6.18	2.90	22.4	11.5	116	113	260
	St. Dev.^{w}	2.63	1.27	11.3	1.68	0.81	7.22	4.10	42.2	24.9	86.7
	Statistic	^{z}EC$_{1:1}$	EC$_{1:5}$	EC$_{e}$	^{y}TDS$_{1:1}$	TDS$_{1:5}$	TDS$_{e}$	SAR^{x}	Na^{+}	Ca^{2+}	Mg^{2+}
			------- dS m^{-1} -------			----------- g l^{-1} -----------			------- meq l^{-1} -------		
Site 2	Mean	9.38	4.11	41.5	6.00	2.63	26.5	42.4	269	101	36.4
	Median	6.92	3.46	23.6	4.43	2.21	15.1	45.6	198	47.7	34.6
	Minimum	4.44	1.84	14.9	2.84	1.18	9.54	15.1	99.7	5.91	4.38
	Maximum	23.3	11.5	105	14.9	7.37	67.3	71.7	785	868	132
	St. Dev.^{w}	5.19	2.56	28.7	3.32	1.64	18.4	18.0	185	216	31.6
	Statistic	^{z}EC$_{1:1}$	EC$_{1:5}$	EC$_{e}$	^{y}TDS$_{1:1}$	TDS$_{1:5}$	TDS$_{e}$	SAR^{x}	Na^{+}	Ca^{2+}	Mg^{2+}
			------- dS m^{-1} -------			----------- g l^{-1} -----------			------- meq l^{-1} -------		
Site 3	Mean	10.7	4.91	52.1	6.84	3.14	33.3	28.6	304	95.7	121
	Median	8.01	3.54	31.7	5.13	2.27	20.3	12.7	141	76.8	120
	Minimum	4.24	2.44	16.4	2.71	1.56	10.5	7.06	71.8	50.1	54.1
	Maximum	20.1	9.33	125	12.9	5.97	79.7	70.5	828	193	192
	St. Dev.^{w}	5.56	2.52	36.1	3.56	1.61	23.1	23.1	263	45.2	49.1
	Statistic	^{z}EC$_{1:1}$	EC$_{1:5}$	EC$_{e}$	^{y}TDS$_{1:1}$	TDS$_{1:5}$	TDS$_{e}$	SAR^{x}	Na^{+}	Ca^{2+}	Mg^{2+}
			------- dS m^{-1} -------			----------- g l^{-1} -----------			------- meq l^{-1} -------		
Site 4	Mean	5.53	2.64	22.1	3.54	1.69	14.2	12.3	120	64.7	44.4
	Median	2.95	1.71	7.9	1.89	1.09	5.06	4.99	24.0	30.9	32.9
	Minimum	0.58	0.31	1.32	0.37	0.20	0.84	0.390	1.12	9.44	3.68
	Maximum	20.9	9.28	106	13.4	5.94	67.6	41.1	624	353	192
	St. Dev.^{w}	5.84	2.56	29.0	3.74	1.64	18.5	14.7	181	79.8	50.5
	Statistic	^{z}EC$_{1:1}$	EC$_{1:5}$	EC$_{e}$	^{y}TDS$_{1:1}$	TDS$_{1:5}$	TDS$_{e}$	SAR^{x}	Na^{+}	Ca^{2+}	Mg^{2+}
			------- dS m^{-1} -------			----------- g l^{-1} -----------			------- meq l^{-1} -------		
Site 5	Mean	5.33	2.50	22.1	3.41	1.60	14.1	11.6	102	71.4	61.3
	Median	4.77	2.33	16.1	3.05	1.49	10.3	9.76	80.4	51.4	39.2
	Minimum	0.34	0.16	0.41	0.21	0.10	0.26	0.53	1.08	1.51	3.93
	Maximum	16.2	7.39	78.8	10.4	4.73	50.4	23.0	330	271	214
	St. Dev.^{w}	3.87	1.67	19.6	2.48	1.07	12.5	7.96	89.3	65.3	54.5
	Statistic	^{z}EC$_{1:1}$	EC$_{1:5}$	EC$_{e}$	^{y}TDS$_{1:1}$	TDS$_{1:5}$	TDS$_{e}$	SAR^{x}	Na^{+}	Ca^{2+}	Mg^{2+}
			------- dS m^{-1} -------			----------- g l^{-1} -----------			------- meq l^{-1} -------		
Site 6	Mean	8.45	3.63	36.8	5.41	2.32	23.6	11.4	160	169	123
	Median	7.16	2.86	27.5	4.58	1.83	17.6	10.4	110	107	86.6
	Minimum	3.32	1.41	8.72	2.12	0.90	5.58	1.66	10.6	41.5	35.3
	Maximum	22.9	9.13	126	14.7	5.84	80.4	24.6	538	646	398
	St. Dev.^{w}	6.01	2.26	34.9	3.85	1.45	22.4	8.28	171	175	106
	Statistic	^{z}EC$_{1:1}$	EC$_{1:5}$	EC$_{e}$	^{y}TDS$_{1:1}$	TDS$_{1:5}$	TDS$_{e}$	SAR^{x}	Na^{+}	Ca^{2+}	Mg^{2+}
			------- dS m^{-1} -------			----------- g l^{-1} -----------			------- meq l^{-1} -------		
Site 7	Mean	5.11	2.43	18.6	3.27	1.55	11.9	6.39	56.4	77.2	74.8
	Median	4.26	1.86	14.2	2.73	1.19	9.11	2.28	17.1	59.8	38.7
	Minimum	2.21	0.79	5.40	1.41	0.50	3.46	0.51	2.97	35.3	23.6
	Maximum	13.8	5.8	57.9	8.83	3.71	37.1	21.4	237	292	312
	St. Dev.^{w}	3.42	1.56	15.2	2.19	1.00	9.71	7.36	71.7	64.0	77.6

^{z}=Electrical conductivity (EC)
^{y}=Total dissolved solids (TDS). Values estimated from measured soil EC as described by (Rhoades, 1996)
^{x}=Sodium adsorption ratio (SAR)
^{w}=Standard deviation (St. Dev.)

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

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

[z]=Electrical conductivity (EC)

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

[x]=Sodium adsorption ratio (SAR)

[w]=Standard deviation (St. Dev.)

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

Study	Equation	r^2	RMSE[z]	Soil Description	EC Range[y]
Chi & Wang (2009)	$EC_e = 11.68(EC_{1:5}) - 5.77$	0.94	7.63	Sandy, Loam, Clay	1 – 227
He et al. (2013)	$EC_e = e^{0.70(\ln EC_{1:5}) + 1.78}$	0.94	27.3	Sandy, Loam, Clay	0 – 20
Hogg & Henry (1984)	$EC_e = 1.56(EC_{1:1}) - 0.06$	0.96	27.4	Sandy, Loam, Clay	0.10 – 42.0
Hogg & Henry (1984)	$EC_e = 3.01(EC_{1:1}) + 0.06$	0.96	15.9	Sandy	0.10 – 22.4
Hogg & Henry (1984)	$EC_e = 3.01(EC_{1:1}) - 0.77$	0.96	16.3	Loam	0.25 – 42.0
Hogg & Henry (1984)	$EC_e = 2.66(EC_{1:1}) - 0.97$	0.96	19.1	Clay	0.28 – 25.7
Khorsandi & Yazdi (2011)	$EC_e = 5.40(EC_{1:5}) - 0.61$	0.94	20.5	Sandy, Loam, Clay	0.48 – 171
Khorsandi & Yazdi (2011)	$EC_e = 1.56(EC_{1:1}) - 0.06$	0.96	27.4	Sandy, Loam, Clay	0.48 – 171
Sonmez et al. (2007)	$EC_e = 7.68(EC_{1:5}) - 0.16$	0.94	12.9	Sandy, Loam, Clay	0.22 – 17.7
Sonmez et al. (2007)	$EC_e = 2.23(EC_{1:1}) - 0.58$	0.96	22.3	Sandy, Loam, Clay	0.22 – 17.7
Ozcan et al. (2006)	$EC_e = 5.97(EC_{1:5}) - 1.17$	0.94	18.9	N/A[x]	N/A
Ozcan et al. (2006)	$EC_e = 1.93(EC_{1:1}) - 0.57$	0.96	24.7	N/A	N/A
USDA (1954)	$EC_e = 3.00(EC_{1:1})$	0.96	15.9	N/A	N/A
Zhang et al. (2005)	$EC_e = 1.79(EC_{1:1}) + 1.46$	0.96	24.6	N/A	0.1 – 108
Klaustermeier et al. (2016)	$EC_e = 10^{[1.2562 (\log EC_{1:5}) + 0.7659]}$	0.97	7.62	Sandy, Loam, Clay	0.4 – 126
Klaustermeier et al. (2016)	$EC_e = 10^{[1.2533(\log EC_{1:1}) + 0.3533]}$	0.94	6.13	Sandy, Loam, Clay	0.4 – 126

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

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

[x] = Data not available

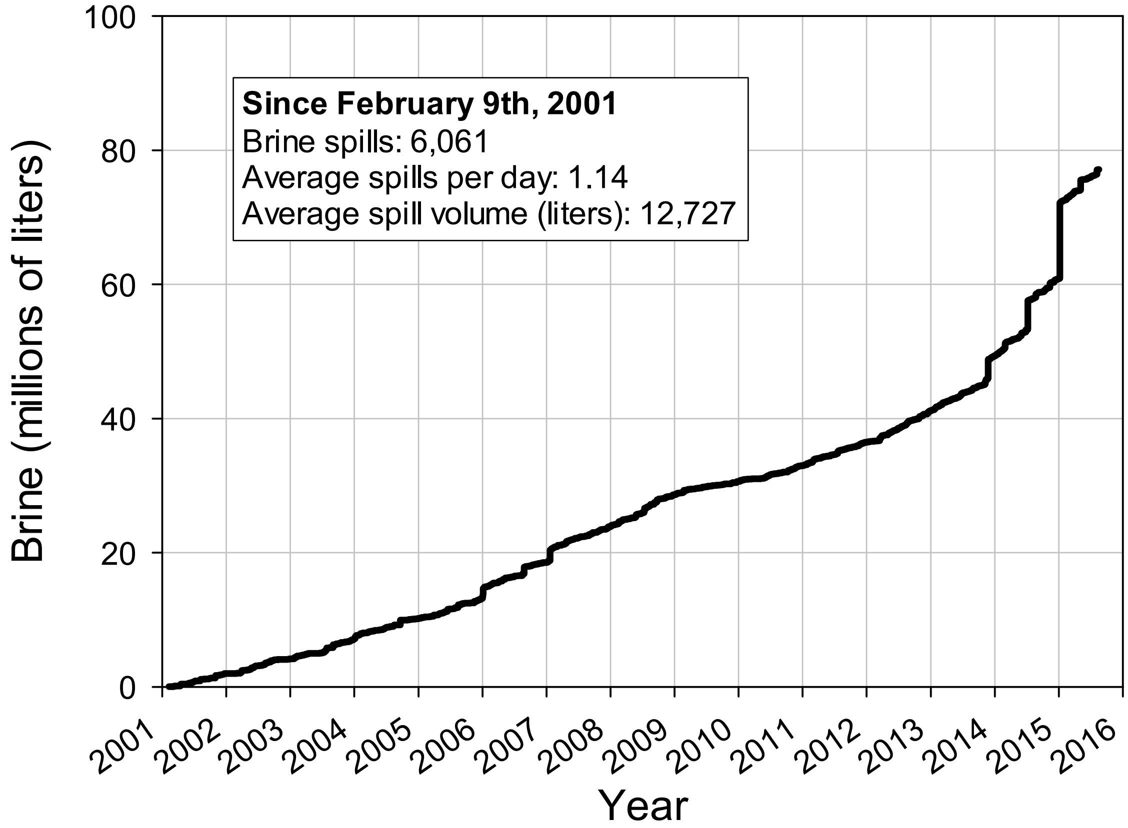

Figure 1. Cumulative brine spilt on and off oil drill pads during and after oil and gas exploration efforts in North Dakota from February 9th 2001 through August 20th 2015 summarized from the North Dakota Department of Health spill database. The first date coincides with when the North Dakota spill records began reporting the amount of brine spilled.

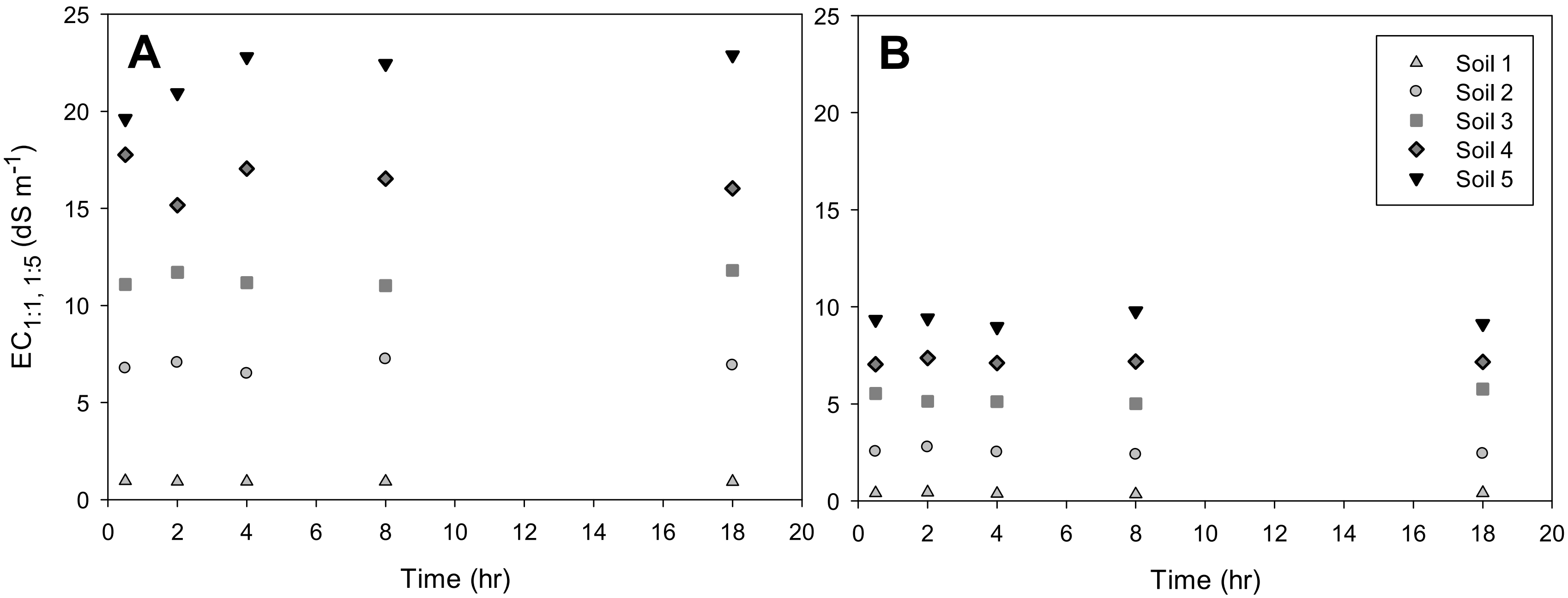

Figure 2. Equilibration times for $EC_{1:1}$ and $EC_{1:5}$. Time periods ranged from 0 to 18 hr. Soil EC values did not differ with time ($P >$ 0.20). Panels A and B are $EC_{1:1}$ and $EC_{1:5}$, respectively.

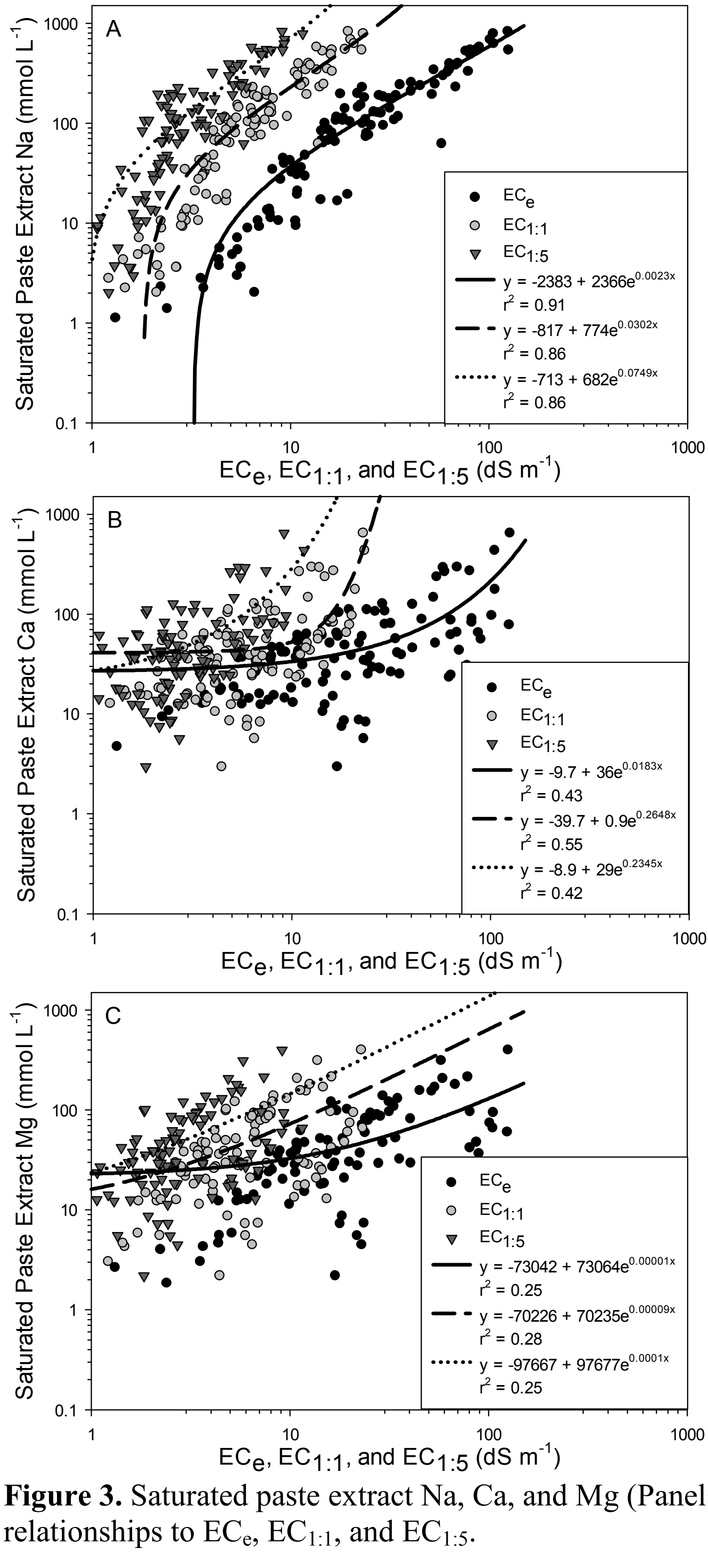

Figure 3. Saturated paste extract Na, Ca, and Mg (Panels A, B, and C, respectively) and their relationships to EC$_e$, EC$_{1:1}$, and EC$_{1:5}$.

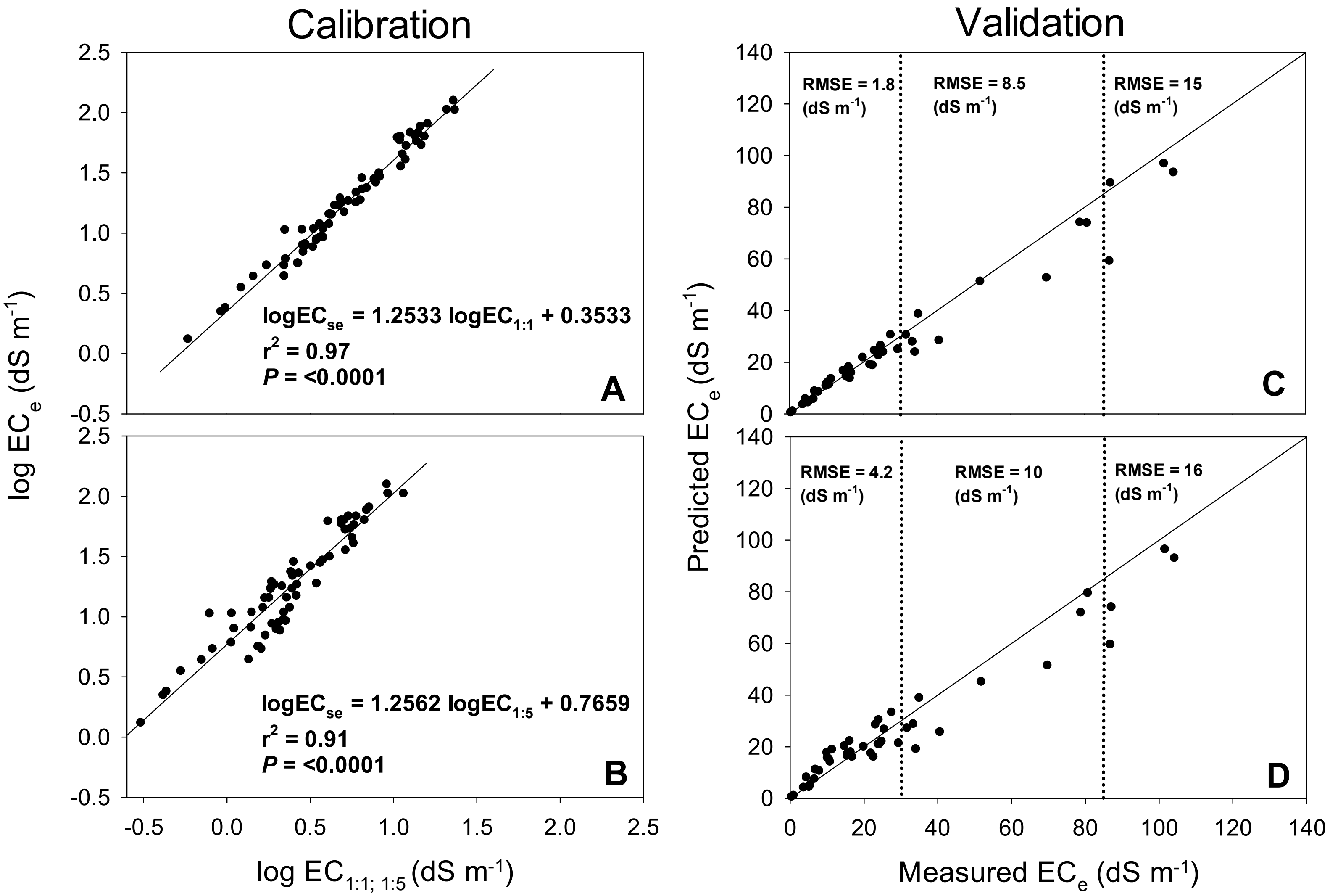

Figure 4. Equation development and validation for EC$_e$ vs. EC$_{1:1}$ and EC$_{se}$ vs. EC$_{1:5}$. Panels A and B are the equation developments for EC$_e$ vs. EC$_{1:1}$ and EC$_e$ vs. EC$_{1:5}$, respectively. Panels C and D are the validations for EC$_{1:1}$ and EC$_{1:5}$ conversion equations, respectively.

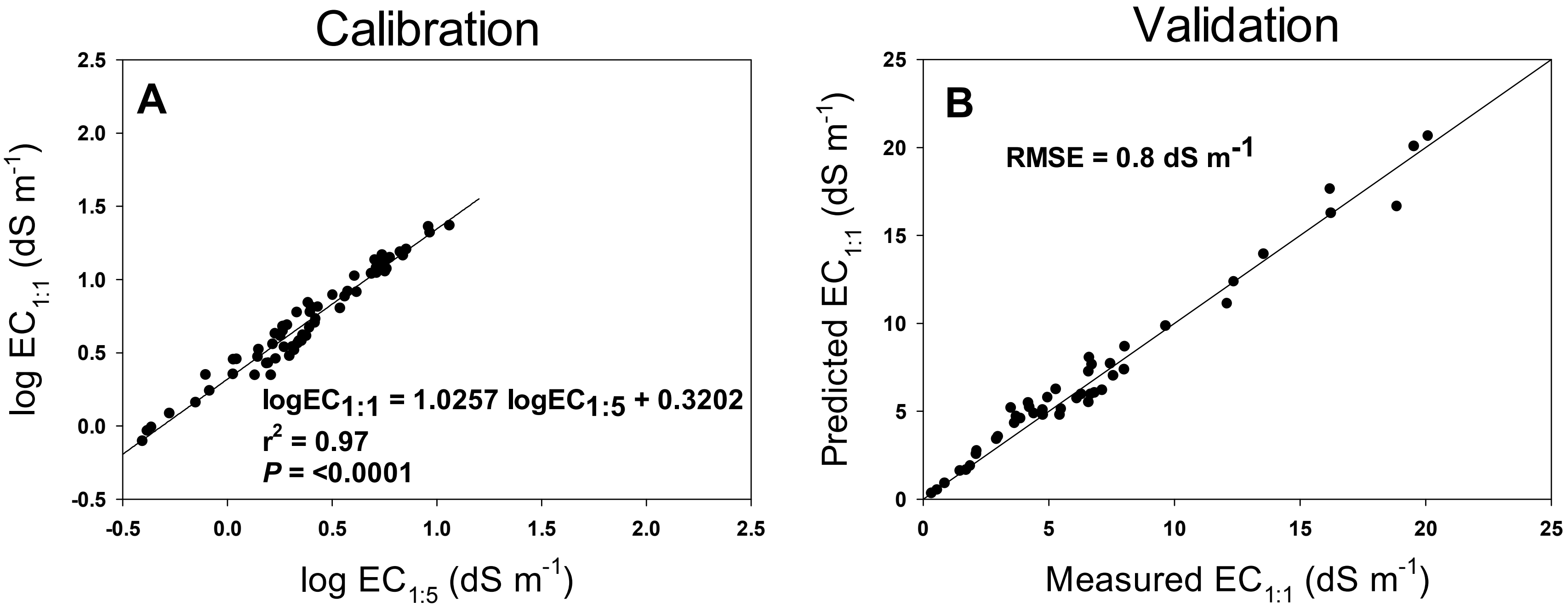

Figure 5. Equation development and validation for $EC_{1:1}$ vs. $EC_{1:5}$. Panel A is the equation development for $EC_{1:1}$ vs. $EC_{1:5}$. Panel B is the validation for the $EC_{1:5}$ conversion equation.

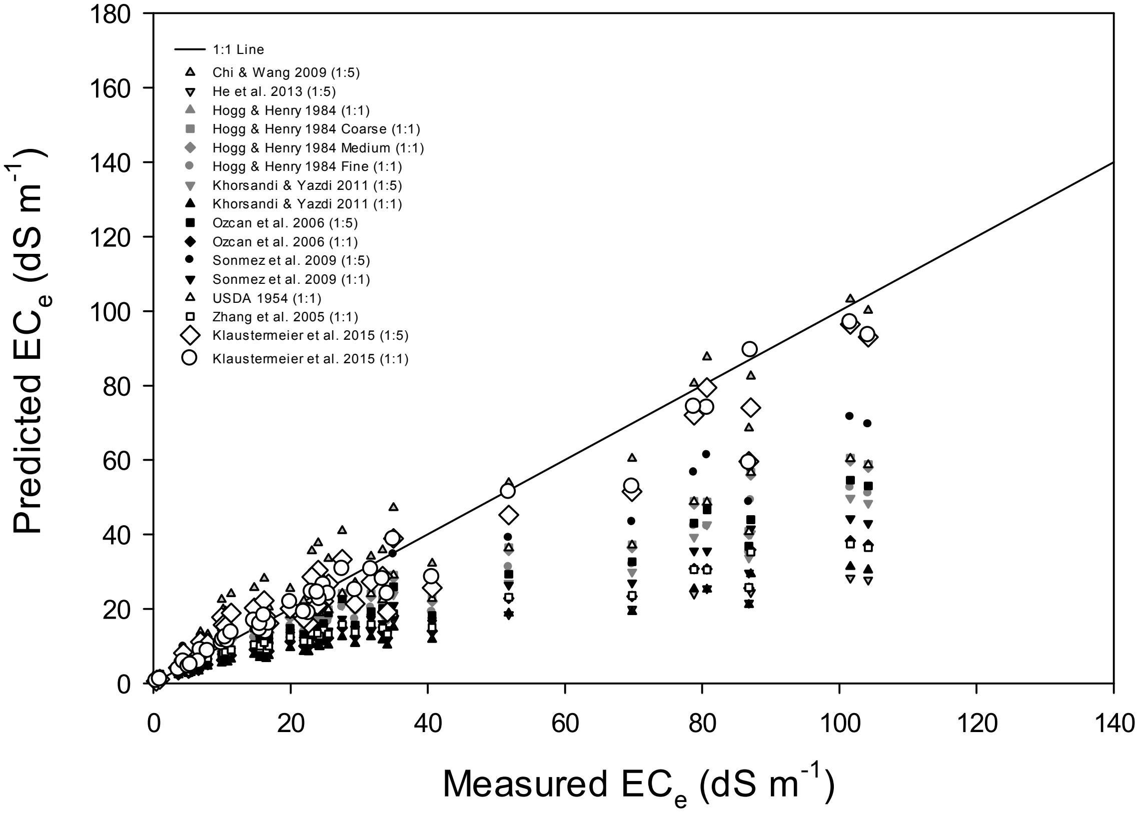

Figure 6. Comparison of 17 developed EC_e conversion equations from nine previous soil salinity studies to those developed in this study. Measured values are from a set of 44 validation soil samples. Circles (gray and black) indicate EC_e predictions based on our newly developed $EC_{1:5}$ and $EC_{1:1}$ conversion equations.

APPENDIX C

BRINE IMPACTED SOILS IN SEMI-ARID LANDS: ELECTRICAL CONDUCTIVITY PLANT THRESHOLDS AND EX SITU/IN SITU REMEDIATION COMPARISONS

BRINE IMPACTED SOILS IN SEMI-ARID LANDS: ELECTRICAL CONDUCTIVITY PLANT THRESHOLDS AND EX SITU/IN SITU REMEDIATION COMPARISONS

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ABSTRACT

Brine is a by-product of oil and gas extraction process that can cause drastic changes to soil chemistry and plant communities when discharged onto the soil surface. Brine spill remediation aims to remove or minimize the saturated paste electrical conductivity (EC_e) to levels suitable for plant growth. My research focused on evaluating residual brine salts and plant parameters using topsoil excavation and chemical amendment techniques, and examining brine thresholds of nine mixed-grass prairie species. Salt tolerant species had higher brine thresholds (between 18.6 and 34.6 dS m^{-1}) than less salt tolerant species (between 9.70 and 18.6 dS m^{-1}). The halophytic species examined in this study were suitable for revegetating remediated brine spill sites. Soil EC_e was not different ($p \geq 0.05$) between remediation techniques to the 60 cm depth. Biomass for all functional plant groups, with the exception of native forb, was not different ($p \geq 0.05$) between remediation techniques. Both techniques were successful at reducing soil EC_e to facilitate natural and assisted vegetation recovery.

GENERAL INTRODUCTION

Oil and gas production can increase the presence of anthropogenic surface salinity through accidental or deliberate discharge of oil-produced water (i.e. brine) onto the soil surface. Brine is a by-product of oil and gas extraction process and contains high concentrations of sodium chloride (NaCl) salts that overwhelm plants' ability to process large quantities of salt ions and maintain a favorable cell-water gradient in the presence of osmotic stress. High concentrations of NaCl lead to ion toxicity, cell dehydration and plasmolysis that ultimately result in plant death. Brine negatively influences vegetation as it lowers the osmotic potential in soil water, which makes it difficult for plant roots to extract water and essential nutrients from the soil matrix. Excess Na^+ ions impede vegetation establishment by weakening aggregate stability and reducing hydraulic conductivity. Brine spill remediation through topsoil excavation (*ex situ*) or chemical amendment (*in situ*) techniques aim to remove or minimize the abiotic stressor to levels suitable for plant growth. The establishment of halophytes post remediation may provide additional protection from the rise of salt-laden water and continuous vegetation cover on remediated brine spill sites.

Halophytes represent a unique group of plant species that can tolerate high salt concentrations ($\geq$ 15 dS m^{-1}; Keiffer and Ungar 2001), — concentrations that would otherwise kill 99% of neighboring species (Flowers and Colmer 2008). Salt-rich environments exert high selection pressures and enable halophytes to develop morphological and anatomical characteristics to cope with salt stress (Flowers et al. 2010). However, abrupt increases in soil salinity, such as brine spills, overwhelm both glycophytes' and halophytes' ability to cope with large amounts of salt at one discrete time. These brine salts kill plants shortly after coming into contact with live plant parts (Murphy et al. 1988; Aschenbach 2006; Aschenbach and Kindscher 2006). Plants die because they are unable to maintain favorable cell-water relations (i.e. turgor) and transport salt ions at a fast enough pace into plant cell vacuoles at high salt concentrations (Flowers et al. 1977; Shavrukov 2013). Brine spill remediation aims to remove or minimize the amount of brine salts to facilitate establishment of plant species. Assisted reintroduction of halophytic species through reseeding treatments on remediated brine spill sites may stabilize soil and provide continuous vegetation cover in the presence of recalcitrant brine salts.

Remediation is essential for improving the physico-chemical properties of contaminated soil to enhance growing conditions for plants (Wong 2003), and it should occur as soon as possible to prevent contaminants from permeating through soil layers (Harris et al. 2005). Topsoil excavation is an *ex situ* method that permanently reduces the amount of contaminated soil onsite by moving it to a new location, such as a landfill. Alternatively, environmental consultants and oil and gas personnel use chemical amendments, such as calcium-based salts, with water to displace sodium (Na^+) and allow for its leaching to lower soil depths. However, this method, without a supplemental water source, is often intensive and ineffective in semi-arid to arid climates (Jury and Weeks 1978; Keiffer and Ungar 2001; Ammari et al. 2013), where limited precipitation prevents ions from leaching below the plant root zone (Keiffer and Ungar 2002). Unfortunately, the majority of high oil-producing regions are located in semi-arid and arid regions in the Great Plains of North America (Keiffer and Ungar 2001), such as western North Dakota. My research aims to evaluate brine thresholds of northern mixed-grass prairie species and evaluate efficacy of *ex situ* and *in situ* remediation techniques.

CHAPTER 1: LITERATURE REVIEW

Natural Abiotic Stressors and Biotic Disturbances

Natural abiotic and biotic factors exerted strong selective pressure on grassland flora that contributed to spatial and temporal heterogeneity in the northern mixed-grass prairie (NMGP) (White 1979; Sousa 1984; Pickett and White 1985). The most influential abiotic factors affecting vegetation composition and productivity in grassland biomes are temperature and precipitation gradients (Mitchell and Csillag 2001; Fredlund and Tieszen 1994). Additionally, small-scale factors such as soil texture, hydrology, nutrients, and natural salt deposits are important for the separation of distinctive plant groups that occupy a variety of microhabitat niches (Keith 1958; Barnes and Harrison 1982; Tilman 1994). The historic presence of biotic disturbances such as fire and grazing, altered vegetation structure to maintain a grassland dominated ecosystem (Collins and Barber 1986; Fuhlendorf and Engle 2004; Davies et al. 2009). The long-term influence of both abiotic and biotic environmental factors resulted in the natural selection of different plant strategies to persist in these habitats (White 1979; Fuhlendorf et al. 2009; Bui 2013).

The vegetation within the NMGP evolved under a system of frequent fires and herbivore grazing (Axelrod 1985; Collins and Barber 1986; Fahnestock and Detling 2002; Janis et al. 2002). Biotic disturbances, such as fire and grazing, resulted in subtle or abrupt changes in ecosystem structure and community. These historic disturbances were beneficial to grassland ecosystems because they removed stagnant biomass, thus stimulating forage regrowth (Johnson and Matchett 2001). Higher forage quality after a burn attracted bison and other herbivores to these areas (Bonham and Lerwick 1976; Coppedge and Shaw 1998). The patchiness of fire followed by grazing created a shifting mosaic of vegetation patches, which provided habitat to a variety of prairie fauna (Vinton et al. 1993; Fuhlendorf and Engle 2004; Fuhlendorf et al. 2009). These keystone processes were largely removed from grassland ecosystems following the European settlement (Knapp et al. 1999; Fahnestock and Detling 2002). Native plants did not evolve at a fast enough pace to effectively compete or survive in these human-altered ecosystems. This human-plant relationship is particularly apparent when examining plants' response to anthropogenic soil salinity.

Saline Seep Formation

The European settlers converted productive grasslands into agriculture farmland by the late 1800's. The change in historical land cover increased the evapotranspiration rate near the soil surface, which consequently increased the development of saline seeps throughout the northern Great Plains (Miller et al. 1981; van Schilfgaarde 1981; Timpson and Richardson 1986). The natural salt deposits in saline seeps are common abiotic stress in semi-arid climates where evaporation exceeds precipitation (Brown 1971; Miller et al. 1981). Saline seeps develop when water carrying dissolved salts from weathered geologic materials, predominantly mixed Na-Mg-Ca-(SO_4) minerals, percolate through the soil profile until it reaches impermeable soil layers (rock or limestone; Miller et al. 1981; van Schilfgaarde 1981; Timpson and Richardson 1986; Timpson et al. 1986). The layers restrict downward water movement, allowing soluble salts to only travel laterally with subsurface water and accumulate in depositional areas (Miller et al. 1981). The soluble salts gradually seep towards the surface through capillary action, especially during dry summer months when soil water travels upward to meet atmospheric evaporative demands (Miller et al. 1989). Furthermore, natural precipitation is limited in semi-arid and arid regions (< 25 cm yr.$^{-1}$) (Keiffer and Ungar 2001; Keiffer and Ungar 2002). This prevents soluble salts from leaching to depths below the root zone. Wet and dry cycles increase salt accumulation near the soil surface, which accelerate saline seep formation and intensify soil salinity. Plants negatively respond to high concentration of salts in the center of saline seeps by decreasing plant growth and future plant recruitment, which lead to increases in bare soil spots.

Salt Stress

Germination is the most critical growth stage in a plants life cycle (Macke and Ungar 1971). Reducing salt concentrations in the top 15 cm of soil is a prerequisite for successful plant germination on salt-affected soils (Chapman 1942; Pujol et al. 2000). Surface salts retard germination of many native plant seeds, especially during periods of water scarcity when salts accumulate on the soil surface. Salts influence plant germination by decreasing the osmotic pressure of the soil, which make it increasingly difficult for seeds to extract water from the soil matrix (Ayers 1952; Ungar 1978). The lack of available water leads to permanent damage of seed embryos or osmotic induced dormancy (Ayers 1952; Ungar 1978; Ungar 1995; Keiffer and Ungar 1997). Surges in soil moisture are a dormancy-release factor (Badger and Ungar 1989), creating suitable places for seedlings to emerge on salt-affected sites, such as saline seeps. Therefore, germination typically occurs in early spring or late fall when water is more available to dilute salt concentrations on the soil surface (Chapman 1942, Ungar 1978; McMahon and Ungar 1978). This strategy enables plants to complete critical growth stages during times of reduced soil salinity prior to periods of increased salt stress (Singh et al. 1983; Schwarz and Redmann 1990; Keiffer and Ungar 2002).

Excessive soluble salts in the soil medium restrict plant growth at the cellular and whole level (Hasegawa et al. 2000). Salts within the root zone induce osmotic stress, disrupt metabolic homeostasis and ion distribution (Serrano et al. 1999; Zhu 2001), and damage important plant tissue through cell plasmolysis (Shavrukov 2013), which can all decrease plant productivity or induce plant death. Salt affected soils impact vegetation by altering the osmotic gradient between soil and plants. Lower osmotic potential in soil water increases the hydraulic gradient towards salt-rich areas and away from plant roots (Bernstein 1975; Shavrukov 2013). Additionally, the decline in osmotic potential alters the uptake and transport of water and essential plant nutrients (NO_3^-, H_2PO_4, K^+, Ca^{2+}) through the cell membrane of plant roots, leading to nutrient deficiencies and ion imbalances (Munns and Termaat 1986; Hu and Schmidhalter 2005). Plants that exhibit salt stress may attempt to regulate water loss by closing stomata cells to limit gas diffusion (carbon dioxide (CO_2)) through plant leaves, preventing photosynthesis from occurring (Longstreth and Nobel 1979; Chaves et al. 2009). Prolonged salt stress prevents plants from re-opening stomata cells and taking in CO_2, which is necessary to produce photosynthetic energy to sustain metabolic activity, leading to plant death. However, some plant species are less sensitive to increases in soil salinity (Bernstein and Hayward 1958; Ungar 1995; Pujol et al. 2000).

Halophytes

Scholars have recognized salt tolerance as a plant trait for more than 200 years (Flowers et al. 1986). Flowers et al. (2010) estimates there are over 350 salt tolerant plant species (i.e. halophytes) that can complete their lifecycle in at least 20 dS m^{-1} (Flowers et al. 2010). Halophytic species evolved in salt-rich environments (e.g., saline seeps, coastal wetlands, and salt plains) where they developed morphological and anatomical characteristics to cope with salt stress (Flowers et al. 2010). Halophytes are able to exclude, regulate, or transport salt ions to maintain homeostasis and ion distribution in the presence of salt stress (Flowers et al. 1977; Salt et al. 1998; Zhu 2003). Plants can survive salt stress by remobilizing water and nutrients to younger leaves and by storing salt ions in older, less productive leaves to complete their life cycle (Munns 2002; Munné-Bosch and Alegre 2004; Munns 2005). Older plant leaves are also more susceptible to salt accumulation in leaf vacuoles because they have been transpiring longer, thus bringing salt ions into leaf vacuoles, and reaching storage capacity sooner than younger plant leaves (Munns 2002). Exceeding the storage capacity in plant cell vacuoles can cause these vacuoles to rupture and leak salt ions into the plant cytoplasm where they become toxic to plant cell enzymes, and/or build up in the surrounding plant cell wall, leading to cellular dehydration (Munns and Passioura 1984; Flowers and Yeo 1986; Munns 2002). Compared to younger plants, older plant species have more plant tissues to transport and store salt ions in leaf vacuoles, which is generally why salt tolerance generally increases with age of plant. However, salt sensitivity can also increase right before reproductive stages when plant resources are allocated to support reproductive structures (Läuchli and Grattan 2007; Oliveira et al. 2013). Some plant species may attempt to accelerate phenological development or switch between sexual and asexual reproduction as a last effort to pass on genetic material (Adams 1990; van Zandt et al. 2003). This survival tactic may produce sterile offspring, reducing the long-term sustainability of their population in salt-affected areas.

Halophytes stabilize and desalinate soils and may act as ecological proxies to replace salt sensitive species (i.e. glycophytes). Native halophytes are preferable over exotic halophytes because native halophytes are usually restricted to native habitats and are adapted to colonizing and completing their cycle in hypersaline environments, such as saline seeps (Flowers et al. 2008; Flowers et al. 2010). Halophytes can remove and contain salt ions and other industrial solutes (e.g., boron (B), cadmium (Cd^{2+}), zinc (Zn^{2+}), lead (Pb^{2+}), and copper (Cu^{+} & Cu^{2+}; Rozema et al. 1992; Manousaki and Kalogerakis 2011) by metabolizing them in plant tissues (Salt et al. 1998). These plants can accumulate contaminants in plant roots and shoots, but removal usually only occurs for the above ground portion (Keiffer and Ungar 2002). Harvesting halophytes above ground biomass at the end of the growing season can permanently reduce soil contaminants to create a conducive environment and favor the establishment of less salt tolerant plant species (i.e. glycophytes) (Salt et al 1995; Salt et al. 1998; Manousaki and Kalogerakis 2011). Most importantly, halophytes stabilize soil in salt-rich environments to prevent further degradation. Belowground roots play an important role in increasing hydraulic conductivity and providing a surface area for microbial communities (Anderson et al. 1993; White et al. 2003).

Halophytes are preferential for revegetating salt-affected sites because they provide additional protection from the gradual rise of salt-laden water during periods of dryness (Barrett-Lennard, 2002; Rabhi et al. 2009; Lokhande and Suprasanna 2012). Although halophytes are beneficial for restoring the biotic processes in salt-affected areas, they are less adaptive to sudden increases in soil salinity (Shavrukov 2013). Plants are not likely to recover even if removal of salts occurred shortly after introduction into the growing medium (Shavrukov 2013). Oil-produced water (i.e., brine) spills from oil and gas development occur suddenly and result in unprecedented amounts of anthropogenic surface salts throughout the Great Plains (Aschenbach and Kindscher 2006).

Anthropogenic Salinity: Brine

Improvements in oil and gas technology have increased access to shale reservoirs and consequently these improvements have increased the amount of brine produced in North America (Rahm 2011; Mason 2012; Brantley et al. 2014). Hydraulic fracturing— also known as hydrofracturing — is a process in which water, sand, and additive chemicals travel at high pressure through an underground wellbore, creating micro fractures in the permeable rock, releasing trapped oil and gas (Brantley et al. 2014). Sand particles prop-open crevices in the shale, allowing water and solvents to travel through the permeable shale rock. The shale formation contributes large amounts of dissolve salts (Meissner 1978; Whittig et al. 1982). These salts mix with water to create brine that travels back to the soil surface during oil and gas production (Harkness et al. 2015). Brine is a regulated waste by-product of the oil and gas extraction process. Brine is usually stored in tank battery containers where it is recycled, transported, or permanently re-injected into underground storage facilities (Brittingham et al. 2014).

Brine spills are arguably the most environmentally destructive and controversial aspect of the oil and gas extraction process (Jager et al. 2005; Aschenbach and Kindscher 2006). Sodium chloride (NaCl) comprises 90% of brine salts and can have a saturated paste electrical conductivity (EC_e) magnitude (≤ 200 dS m^{-1}) higher than saline seep concentrations (≥ 15 dS m^{-1}) (Merrill et al. 1990; Jong 1982; Keiffer and Ungar 2002; Aschenbach and Kindscher 2006). Brine contamination occurs when there is a tank battery overflow, pipeline leak, or migration of salts from a reserve pit (Keiffer and Ungar 2002; Sublette et al. 2007). These types of uncontrollable releases leave permanent marks on the landscape (Jager et al. 2005), which can persist for decades in semi-arid to arid regions in the absence of remediation techniques.

Brine spills are a severe abiotic site modification that can have long lasting impacts on soil and vegetation parameters. Salts from brine spills are considered especially problematic because they are both saline and sodic ($EC_e \geq 4$ dS m^{-1} and SAR > 13) (USDA, 1954). Excessive Na^+ ions can lead to dispersion of clay particles on soil aggregates, thus weakening soil structure and resulting in reduced hydraulic conductivity. Additionally, salts near the soil surface sterilize the soil seed bank and prevent successful plant migration from nearby propagules (Ungar 1978; Keiffer and Ungar, 1977; Ungar 1995; Ungar 2001; Keiffer and Ungar 2002). The high concentrations of salts in brine require an active approach to speed-up natural processes towards a predefined state. Brine spill remediation aims to remove or minimize the abiotic stressor to increase the success rate of both natural and assisted plant reintroduction. The goal of remediation is to reinstate some ecological processes to assist in the long-term sustainability of the site. Reduction of salt concentrations through *ex situ* and *in situ* remediation techniques is the first step towards creating a more conducive environment for soil and plant organisms.

Ex-Situ and In-Situ Brine Spill Remediation

Topsoil excavation (*ex situ*) permanently reduces the volume, toxicity, and mobility of contaminants (Steele and Pichtel 1998). The physical removal of contaminants to an approved disposal location decreases off-target effects and future liability (Steele and Pichtel 1998). Although this technique is effective in reducing the inhibitory effect of brine salts and other industrial effluents, the removal of soil contaminants and introduction of replacement soil destroys thousands of years of soil development (Bradshaw 1997). Replacement soil also poses its own ecological implications because it may unintentionally contain exotic seeds in the soil seed bank that may germinate and spread into the surrounding area. Furthermore, new topsoil may differ in soil chemical and physical properties (eg. soil texture, nutrients, organic matter) and may yield a different plant community than what previously existed before the spill. The permanent loss of the original soil source and lack of adequate soil structure associated with the topsoil excavation technique increases soil erosion and decreases soil porosity when replacement soil is mechanically compressed (Stylinski and Allen 1996; Angers and Caron 1998), which can negatively influence plant root growth (Milchunas et al. 1999; Stylinski and Allen 1996; Pagliai et al. 2004). Roots unable to grow and develop lead to declines in microbial activity, nutrient reserves, and moisture availability (Bronick and Lal 2005). The lack of plant inputs reduces overall soil fertility. The loss of original soil structure is defendable only when contamination poses a significant threat to human and/or environmental health (Wilson and Jones 1993; Efroymson et al. 2004).

Alternatively, chemical amendments (*in situ*) are a common practice to remediate salt-affected soils and minimally disrupt soil integrity. The minimal disruption of the original soil has a greater public acceptance among soil and ecologists because it does not transport contaminated soil from one place to another (Khan et al. 2000). Chemical amendments are typically calcium (Ca^{2+}) based salts, such as gypsum ($CaSO_4^{2-} \bullet 2H_2O$) and calcium chloride ($CaCl_2$), to replace sodium ($Na^+$) ions from soil exchange sites and move them from upper to lower soil depths (Gharaibeh et al. 2009; Mahmoodabadi et al. 2013; Ammari et al. 2013). Calcium based salts differ from Na^+ based salts because they flocculate clay particles (Peterson 1948), as opposed to Na^+ ions, which disperse clay particles. Divalent cations (Ca^{2+}) replace monovalent cations like Na^+ ions because they have a higher affinity to bond with negatively charged sites on soil particles (Alva et al. 1991; Gharaibeh et al. 2009). This technique requires water to facilitate Na^+ exchange because it favors the adsorption of Ca^{2+} ions to displace and leach Na^+ ions (Reeve and Bower 1960). Preliminary studies estimate a 100:1 dilution ratio of fresh water to brine salts to permit plant growth on brine-affected soils (Munns and Stewart 1989). Jury and Weeks (1978) estimate that the leaching process for chemical amendments can take upwards of 3,000 years depending upon soil texture and exchangeable sodium percentage (Jury and Weeks 1978; Taylor et al. 1999; Harris et al. 2005). The process in which chemical amendments displace lower valence cations (Na^+) with higher valence cations (Ca^{2+}) can lead to a reduction in soil EC and sodium adsorption ratio (SAR) (Reeve and Bower 1960; Hamza and Anderson 2003; Hanay et al. 2004). The rate of Na^+ displacement depends upon soil structure, activity of Ca^{2+} in the soil matrix, and electrolyte concentration of water (Reeve and Bower 1960; Gharaibeh et al. 2009).

Although chemical amendments are effective at displacing unwanted salt ions, they may also indiscriminately leach macro and micronutrients to lower soil depths where they are inaccessible to plant roots (Yazdanpanah et al. 2012). This remediation technique is not suitable in the presence of a shallow water table, where displaced salt ions and additive brine chemicals can inadvertently contaminate groundwater. Furthermore, chemical amendments such as gypsum are only effective at the depth of application, requiring some surface disruption to incorporate the amendment to lower soil depths (Jong 1982; Robbins 1986).

Organic materials serve a dual purpose by providing protection from erosional processes and improving the soil conditions for revegetation of salt-affected soils (Wong 2003; Tejada et al. 2006; Tejada et al. 2009). Organic materials are organic waste products from living organisms such as plants and/or animals. Coupling organic amendments with remediation techniques reduces erosional hazards on newly disturbed soil and increases the efficacy of Na^+ leaching. A study using a subsurface draining system and hay decreased brine salts ($NaCl$) by an average 93 and 78% after a four year period, with hay playing an important role in limiting the rate of evaporation from the soil surface to enhance salt leaching (Harris et al. 2005). Several other studies observed similar results using organic materials to desalinate surface salts (Dorado et al. 2003; Wong 2003, Zhang et al. 2008). Organic materials increase percent organic matter that binds humic colloids together (Dorado et al. 2003), promoting microbial activity and soil structure formation (Roldán et al. 1996; Bulluck et al. 2002; Liang et al. 2003; García-Orenes et al. 2005; Tejada et al. 2006; Tejada et al. 2009; Diacono and Montemurro 2010). Additionally, organic amendments replenish nutrients lost by leaching to improve soil fertility and facilitate revegetation of saline-sodic soils (Liang et al. 2003; Tejada et al. 2009; Yazdanpanah et al. 2012). Organic additions, such as wood chips, hay, mulch, straw, wattles, and biodegradable netting my accelerate plant succession by ameliorating edaphic conditions to stimulate succession of human-disturbed sites.

Brine is an abiotic stress (i.e. soil salinity) that exerts a continuous negative impact on soil and plant parameters when spilt on the soil surface during the growing season. Remediation via chemical amendments and topsoil excavation are two common remediation techniques to lower soil salinity. Remediation attempts to lower soil salinity to facilitate revegetation efforts, however, physical disturbances surrounding oil and gas activities further weaken intact plant communities and can delay plant recovery on post-remediated spill sites. Anthropogenic disturbances associated with oil and gas development include roads, vehicle movement, tilling, and trampling (Larson 2003; Efroymson et al. 2004). These disturbances occur daily in the oil fields and can have negative effects (Rapport and Whitford 1999; Borics et al. 2013) on nearby remediated brine spill sites by preventing the plant community from returning to pre-spill conditions. Anthropogenic disturbances disrupt the soil surface to expose available plant resources (e.g., water, light, nutrients, and space resources) that inhibit the establishment of later successional species and promote the continual dominance of early successional species (Grime 1977; Grubb 1977; Daehler 2003).

Plant Succession

Early successional species, such as ruderals and exotics, tend to have small seeds, high dispersal capabilities, and rapid growth (Huston and Smith 1987; Eriksson and Eriksson 1997).

All of these strategies enable early successional species to move and quickly establish on disturbed sites. Common early successional species in the NMGP include foxtail barley (*Hordeum jubatum* L.), curlycup gumweed (*Grindelia squarrosa* (Pursh) Dunal), field brome (*Bromus arvensis* L.), eastern daisy fleabane (*Erigeron annuus* (L.) Pers.), and annual sunflower (*Helianthus annuus* L.). These early successional species are likely to dominate disturbed sites until later competitive, successional species become established (Mcintyre et al. 1995). Succession is the change in vegetation overtime (Huston and Smith 1987). However, the rate of replacement and facilitation of vegetation, such as early successional species by later successional species, may occur more slowly in the presence of soil salinity or when topsoil has been removed (Keiffer and Ungar 2002; Prach and Pyšek 2001).

Short-lived ruderal and exotic species may be benign and even beneficial in the early stages of the reclamation process. Early successional species provide plant nutrients through high species turnover and stabilize lose soil to rebuild soil structure, which facilitate the replacement of later successional species (Tansley 1935; D'Antonio and Meyerson 2002; Ewel and Putz 2004). Later successional species do not readily establish on disturbed sites because they are slower growing and primarily reproduce by vegetative means (Eriksson and Jakobsson 1998). Later succession species also tend to have heavier seeds (Leishman 1999) that are less likely to reach disturbed sites as compared to lighter, smaller seeds of early successional species (Primack 1987; Reader 1993). Differences in plant life histories may create distinct contrasts in plant community assemblages on the bordering edge of native prairie and disturbed sites.

Successional trends on remediated brine spill sites are largely unknown, and perpetual disturbances surrounding these areas can lead to permanent shifts in vegetation cover. Exotics are detrimental to disturbed sites if they are long-lived colonizers that persist in plant communities, ultimately becoming invasive (D'Antonio and Meyerson 2002). Invasive plant species are difficult to eradicate because they compete for the same resources as native plant species, but aggressively take over and create monotypic stands of only a few species (Lesica and DeLuca 1996; Henderson and Naeth 2005; Murphy and Grant 2005; DeKeyser et al. 2015). Common invasive species in the NMGP include Kentucky bluegrass (*Poa pratensis* L.), crested wheatgrass (*Agropyron cristatum* (L.) Gaertn.), Canada thistle (*Cirsium arvense* (L.) Scop.), and leafy spurge (*Euphorbia esula* L.). The long-term occupancy of these invasive species irreversibly change plant community assemblages and make it difficult to reach reclamation objectives (Brandt and Rickard 1994; Stylinski and Allen 1996). Residual brine salts also alter successional sequences by exerting a strong abiotic gradient (i.e. soil salinity) that inhibits salt sensitive species from successfully establishing on these sites. Assisted revegetation using native halophytic species (e.g., *Pascopyrum smithii* (Rydb.) Á. Löve, *Puccinellia nuttalliana* (Schult.) Hitchc., *Sporobolus airoides*, *Distichlis spicata*, and *Hordeum jubatum*) are desirable because they grow naturally in the NMGP and are commercially available (Dodd and Coupland 1966; Braidek et al. 1984). These grass species are also more aesthetically pleasing than early successional species, and the establishment of native halophytic grasses on remediated brine spill sites may help land managers achieve reclamation goals.

Characterizing plant community assemblages and quantifying plant productivity on remediated brine spill sites is useful for determining if remediation was successful at restoring the plant community to pre-spill conditions (Halvorson and Lang 1989). Our research aims to investigate plant community responses to different levels of salinity through a greenhouse study and to quantify residual brine salts and plant establishment on remediated sites in a field study. The objectives of our greenhouse study were to determine brine/plant survival thresholds of nine plant species at five brine-derived soil saturated paste extract (EC_e) levels, and evaluate plant sensitivity at seedling and late vegetative — pre-boot growth stages. Our research will help establish ECe benchmarks as well as identify suitable species for reclamation of remediated brine spill sites for oil and gas personnel and environmental consultants. The objective of the field study was to compare efficacy of the two soil amendment techniques by evaluating remaining brine salts and quantifying plant establishment on remediated spill sites to determine which method is more appropriate for the environmental conditions in semi-arid rangelands.

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APPENDIX D

OIL-PRODUCED WATER THRESHOLDS ON RANGELAND PLANT'S SURVIVAL UNDER GREENHOUSE CONDITION

OIL-PRODUCED WATER THRESHOLDS ON RANGELAND PLANT'S SURVIVAL UNDER GREENHOUSE CONDITIONS

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Abstract

Questions: How does different levels of oil-produced water (i.e. brine) affect both halophytic and glycophytic species?

Methods: We conducted a non-leaching greenhouse experiment on nine plant species at five brine-derived saturated paste electrical conductivities (EC_e; 2, 4, 8, 16 and 32 dS m^{-1}) at seedling (SDLG) and late vegetative — pre-boot (LV) growth stages. Concentrated brine (210 dS m^{-1}) was diluted with distilled to create five EC_e concentrations, with no added brine as the control, and applied to five pots per EC_e treatment in a loam soil. Thirty days after brine application, we collected survival and biomass data on greenhouse plants and analyzed with regression.

Results: Halophytic and glycophytic plants exhibited increased mortality at EC_e greater than 9.7 dS m^{-1}. *Hordeum jubatum* L. and *Puccinellia nuttalliana* (Schult.) Hitchc. survived at the 34.6 dS m^{-1} at both growth stages. Above and belowground biomass declined with each additional EC_e level for all species at both growth stages. Decreases in aboveground biomass ranged from 4 to 60% whereas belowground biomass declined by 4 to 50% when compared to the control treatment for each species across all EC_e levels.

Conclusions: Halophytic species exhibited a brine threshold between 18.6 and 34.2 dS m^{-1}, whereas glycophytic species exhibited a lower EC_e survival threshold (9.70 and 18.6 dS m^{-1}). We did not identify brine thresholds ($\geq$ 34.2 dS m^{-1}) for *Hordeum jubatum* and *Puccinellia nuttalliana*. The halophytic species examined in this paper have different vacuole capacities and

transpiration rates as well as different salt tolerance mechanisms to revegetate salt-affected areas. The halophytic species examined in this greenhouse experiment are suitable candidates to diversify oil and gas reclamation seed mixes.

Introduction

Soil salinity is a major limiting factor to plant productivity, affecting approximately 7% of the earth's land surface (Ghassemi et al. 1995). Both natural and human-induced processes cause soil salinity. Oil and gas production activities, such as the oil production in the Northern Plains, increased the presence of anthropogenic salinity in the Northern Mixed Grass Prairie (NMGP) region with over 78 million liters of oil-produced water (i.e. brine) spilled in North Dakota since 2001 (ND DOH, 2015). Accidental or deliberate discharges of brine adversely affect soil and vegetation parameters, and in the absence of remediation can create areas that are unable retain soil resources to support vegetation (Jager et al. 1995). Salt tolerant plant species (i.e. halophytes) aid in the amelioration of salt-affected sites, but their value as possible candidates to revegetate remediated brine spill sites on western rangelands has not been evaluated in a greenhouse experiment (Aschenbach & Kindscher 2006). This study examines the ability of halophytic and glycophytic cool and warm-season grasses to grow and survive under non-leaching greenhouse conditions at two growth stages.

High salt concentrations impede plant recovery in semi-arid to arid climates where limited precipitation restricts downward leaching of salt ions below the plant root zone. Leached salt-laden water travels upward to the soil surface via capillary action during hot, dry months (Thimm 1990), preventing plant seeds from germinating, and killing seedlings (Ungar 1978; Keiffer & Ungar 1997). This salt migration and subsequent reduction in plant establishment will result in the need for additional soil treatments and reseeding applications. Salt tolerant plant species are better equipped to handle gradual changes in soil salinity. Halophytes have evolved under natural saline environments such as saline seep formations, allowing them to develop morphological and anatomical characteristics to deal with salt stress (Flower et al. 2010). Halophytes maintain plant performance in salt-rich environments ($\geq$ 15 dS m^{-1}; Keiffer and Ungar 2001) by closing stomata cells and accumulating salt ions in leaf vacuoles. Leaf vacuoles will accumulate salt ions until they reach capacity causing them to rupture and leak salt ions into the cell cytoplasm and cell wall, thus leading to cellular dehydration (Munns 2002; Munné-Bosch and Alegre 2004; Munns 2005). Salt tolerance generally increases with age of plant even though older plants have been transpiring for longer and have brought in more salt ions through plant roots (Munns 2002; Munné-Bosch and Alegre 2004; Munns 2005). Mature plants can survive in the presence of salt stress through senescence of older plant leaves first and remobilization of water and nutrients to younger photosynthetically active leaves (Munns 2002; Munné-Bosch and Alegre 2004; Munns 2005). However, salt sensitivity can increase right before maturity when plants allocate resources to support reproductive structures (Läuchli & Grattan 2007; Oliveira et al. 2013). Although halophyte species exhibit higher salt tolerances than less salt tolerant plant species (glycophytes), halophytes are less equipped to handle large doses of salt at one discrete time, leading to cell plasmolysis (Shavrukov 2013).

Cell plasmolysis is the process in salt concentrations build-up to toxic levels in the cytoplasm and leak into the plant cell wall. Cell plasmolysis occurs when there is an abrupt increase in salinity in the growing medium that leaves plants unable to mobilize available resources and initiate survival mechanisms fast enough to combat changing soil conditions (Shavrukov 2013). Plant survival mechanisms include accumulation of ions, solutes, and carbohydrates to aid in osmotic adjustment as well as salt ion exclusion and compartmentalization to maintain ion homeostasis (Munns 2002; Shavrukov 2013). Fortunately, plants rarely experience sudden increases in soil salinity in field conditions (Shavrukov 2013), with the exception of low quality irrigation water and brine spills. Brine (90% NaCl) is a regulated waste product of oil and gas extraction process that contains salt concentration magnitudes higher than natural saline environments (McMillion 1965). Accidental and deliberate discharges of brine kill actively growing plants shortly after coming into contact with plant parts (Murphy et al. 1988; Aschenbach & Kindscher 2006). The loss of stabilizing root structures and protective plant cover leave soil susceptible to erosional hazards. Salts from brine spills also have long-term impacts on soil and vegetation parameters because they alter the osmotic potential energy of soil water making it difficult for plants to colonize brine-affected sites without some type of soil amelioration technique.

Brine spill remediation techniques can remove or minimize the abiotic stressor (salt) to levels suitable for plant growth. Although brine spill remediation can reduce the overall concentration of brine salts, recalcitrant salts can resurface during dry months and result in plant death (Thimm 1990). Halophytes provide short-term protection from the rise of salt-laden water by up-taking salt ions to create a more conducive environment that facilitates the establishment of less salt tolerant plant species (Barrett-Lennard 2002; Manousaki & Kalogerakis 2011). Harvesting of aboveground parts of halophytes at the end of the growing season can also permanently decrease salt concentrations. Additionally, some halophytes can also uptake ions that exceed plant nutrient requirements from industrial solutes containing boron (B), cadmium (Cd^{2+}), zinc (Zn^{2+}), lead (Pb^{2+}), and copper (Cu^{+} & Cu^{2+}; Rozema et al. 1992; Manousaki & Kalogerakis 2011). Halophytes are desirable for reclaiming salt-affected sites because they are naturally present in the environment and commercially available (Aschenbach & Kindscher 2006: Manousaki & Kalogerakis 2011).

Evaluation of salt tolerance includes examining plant survival and growth at different saturated paste electrical conductivity (EC_e) levels. Identifying plant survival thresholds of salt tolerant and sensitive NMGP species at seedling and pre-mature growth stages along an EC_e gradient may provide insight into acceptable EC_e ranges and the type of species that would succeed on newly remediated brine spills in western rangelands. Objectives of this study were to 1) determine plant survival thresholds of nine plant species treated with five brine-derived soil EC_e levels and 2) evaluate plant sensitivity at seedling (SDLG) and late vegetative—boot stage (LV) stages. We hypothesized that plants will exhibit salt sensitivity at concentrations greater than 2 dS m^{-1}, as suggested by preliminary greenhouse trials. We expected plant mortality to increase with each additional brine concentration for SDLG and LV growth stages. Halophytic plant species (*Pascopyrum smithii* (Rydb.) Á. Löve, *Puccinellia nuttalliana* (Schult.) Hitchc. *Sporobolus airoides*, *Distichlis spicata* (L.) Greene, and *Hordeum jubatum* L.) are likely to display higher EC thresholds than less salt tolerant species in this experiment due to salt ion accumulation and avoidance mechanisms.

Materials and Methods

We conducted a greenhouse experiment at the North Dakota State University Agricultural Experiment Station Research Greenhouse Complex in Fargo, North Dakota, USA to evaluate brine thresholds of nine NMGP species. Greenhouse conditions were with a 14:10 hour day:night cycle and a constant temperature (25°C). The growth medium for plants in the experiment was topsoil from a Williams Soil Series (34% clay, 22% silt, 44% sand, and 0.38 dS m^{-1} EC_e). The Williams Series is a moderately, well-drained soil that is the most extensive soil series in western North Dakota and is a suitable soil to study brine and plant relationships. The brine used to derive the soil EC's was collected from a wellhead near the Wiley field in Maxbass, North Dakota. This brine had a 210 dS m^{-1} EC, and sodium (74, 930 parts per million (ppm)), chloride (149,908 ppm), potassium (2,809 ppm), calcium (2,140 ppm), sulphate (1,540 ppm), magnesium (602 ppm), and boron (81.7 ppm) levels (Midwest Laboratories, Inc., Omaha, Nebraska). The plants used to test brine thresholds in this experiment are all native to the NMGP with the exception of Kentucky bluegrass (*Poa pratensis* L.) (Table 1).

Table 1: Reported survival and/or biomass electrical conductivities of saturated paste extract (EC$_e$) thresholds (dS m^{-1}) of nine Northern Mixed-Grass Prairie species at germination, seedling, and mature growth stages.

Species Name	EC Threshold (dS m^{-1})	Reference
Cool Season (C$_3$) Grasses		
Pascopyrum smithii †	10^{G} & 58^{S}	(Moxley et al. 1978; Aschenbach 2006)
Poa pratensis	22^{S}, 3^{S} & $5\text{-}6^{M}$, 23^{S}, & 8^{S}	(Kenkel et al. 1991; Carrow & Duncan 1998; Alshammary et al. 2004; Gilbert & Fraser 2013; Hu et al. 2015)
Hordeum jubatum†	26^{S} & 22^{S}	(Badger &Ungar 1990; Kenkel et al. 1991)
Nassella viridula	$9\text{-}10^{G}$	(Ries & Hofmann 1983)
Puccinellia nuttalliana†	22^{S}, 19^{G}, 23^{S}	(Kenkel et al. 1991; Tarasoff et al., 2007b; Gilbert & Fraser, 2013)
Warm Season (C$_4$) Grasses		
Distichilis spicata†	42^{M}, 66^{M}, 23^{M}, & $35\text{-}41^{M}$	(Ungar 1966; Ungar 1969; Hansen et al. 1976; Alshammary et al. 2004)
Bouteloua gracilis	31^{G} & 16^{G}	(Zhang et al. 2012; Dudley et al. 2014)
Schizachyrium scoparium†	$9\text{-}10^{G}$ & $3\text{-}16^{G}$	(Ries & Hofmann 1983; Dudley et al. 2014)
Sporobolus airoides†	$11\text{-}25^{G}$ & $9\text{-}10^{G}$	(Hyder & Shamsa 1972; Ries & Hofmann 1983)

† = Halophytic species

G = Germination, S = Seedling, M = Mature

We air-dried field soil and sieved it through a 16 mm mesh to remove rocks and debris, then mechanically ground the soil before transferring into 15.2 x 10.8 cm pots (1,450 g per pot) lined with plastic to prevent leaching. Seed germination occurred in vermiculite, and then transplantation of seedling to pots occurred between 7 and 14 days post-germination. Each pot contained two seedlings with five pots per EC treatment for all nine species. Target brine-derived soil EC_e treatments were 2, 4, 8, 16, and 32 dS m^{-1}. The control treatment for each species was no brine (0.38 EC_e). We determined the initial brine-derived soil EC_e by estimating field capacity of the soil using particle size analysis, bulk density, and a pedotransfer function to determine the proportion of concentrated brine (210 dS m^{-1}) to add to each deionized water solution (Saxton & Rawls 2006). The differences in target versus actual soil EC_e (3.3, 5.8, 9.7, 18.6, and 34.6 dS m^{-1}) are attributed to the fact that brine is not a uniform solution but a mixture of petroleum hydrocarbons, industrial effluents, and other soluble salts. Additionally, the EC_e values from the soil do not include ions exchanged onto the mineral surface complexes.

Application of brine-derived soil EC_e concentrations occurred at two different growth stages for each plant species and included 1) seeding stage (SDLG) and 2) late vegetative—pre-boot (LV) growth stage. Assessment of plant survival occurred 30 days after brine application. Survival assessment of individual plants included visually examining green plant parts and creasing plant leaves to observe water transport via xylem to aerial plant parts. Shortly after visual assessment, aboveground and belowground biomass were harvested, separated and oven dried (49 °C) to a constant weight. Data analysis included linear regression models for brine survival thresholds done in SAS® (version 9.3, SAS Institute, Inc., Cary, NC). We then compared first-order regression models (linear, exponential decay, power, growth, sigmoidal, and logistic) using a small-size corrected version of Akaike information criterion (AIC) to select the best model for above and belowground biomass weights in SAS® (version 9.3, SAS Institute, Inc., Cary, NC; Hurvich & Tsai 1989). Significance for all regression models were based on an alpha $p < 0.05$.

Results

Halophytic and glycophytic plant species exhibited salt sensitivity at soil EC's greater than 8 dS m^{-1} under greenhouse conditions (Figure 1 & 2).The two growth stages of halophytic plant species played a minimal role in plant survival at the respective brine-derived soil EC's ($p \geq 0.05$). The most resilient halophytic species in this experiment were *Hordeum jubatum*, *Distichlis spicata*, *Puccinellia nuttalliana* and *Sporobolus airoides* with no tolerance thresholds up to 34.6 dS m^{-1} detected at one or both growth stage(s) (Figure 1 & 2). *Pascopyrum smithii* had approximately 50% and 75% survival at SDLG and LV growth stages at 34.6 dS m^{-1} and less salt tolerant plant species, such as *Poa pratensis*, *Nassella viridula* (Trin.) Barkworth, *Bouteloua gracilis* (Willd. ex Kunth) Lag. ex Griffiths, and *Schizachyrium scoparium* (Michx.) Nash exhibited no plant mortality at soil EC_e less than 9.70 dS m^{-1}.

Aboveground biomass for SDLG and LV growth stage treatments declined by 4 to 60%, with each treatment increase in soil EC for all plant species when comparing differences among treatments as opposed to differences between treatments. Glycophytic species (*Poa pratensis*, *Nassella viridula*, *Bouteloua gracilis*, and *Schizachyrium scoparium*) experienced a 45 to 100% reduction in overall biomass between the 18.6 and 34.6 dS m^{-1} treatments for both growth stages when compared to the control treatment (Figures 3 & 4). Halophytic species also showed a gradual decline in aboveground biomass, but much less than glycophytic species. Overall biomass reduction was higher for *Pascopyrum smithii* at the SDLG growth (84%) than at the LV growth stage (72%) between 34.2 dS m^{-1} as compared to the control treatment. This trend was also similar for overall biomass production of *Hordeum jubatum* (70% (SDLG) & 40% (LV)), *Puccinellia nuttalliana* (77% & 30%), *Distichilis spicata* (49 & 42%), and *Sporobolus airoides* (74%; SDLG only stage) with the largest reduction occurring between 18.6 and 34.6 dS m^{-1} treatments. However, there was no relationship ($p \geq 0.05$) between increasing soil EC and biomass reduction of *Sporobolus airoides* at the LV growth stage.

Belowground biomass for SDLG and LV plants were slightly less than aboveground biomass, declining by 4 to 50%, when comparing differences among treatments as opposed to differences between treatments. Roots exhibited less of a decline with each increase in soil EC_e at both the SDLG and LV growth stages when compared to the aboveground portion (i.e. leaves and stems). Reductions in overall belowground biomass for halophytes and glycophytes mirrored that of aboveground biomass with the lowest difference in reduction occurring between the control (0.38 dS m^{-1}) and 3.30 dS m^{-1} treatment and the largest difference between EC_e 18.6 and 34.6 dS m^{-1} treatments, respectively. SDLG survival and biomass weights was lower than LV plants. The reduction in biomass between the control treatment (0.38 dS m^{-1}) and 34.6 dS m^{-1} was 100% for SDLG and 97% for LV glycophyte plants. Halophytes exhibited lower biomass reduction between 18.6 and 34.6 dS m^{-1} for SDLG (75%) and LV (50%) plants. The results of this greenhouse experiment support our initial hypotheses.

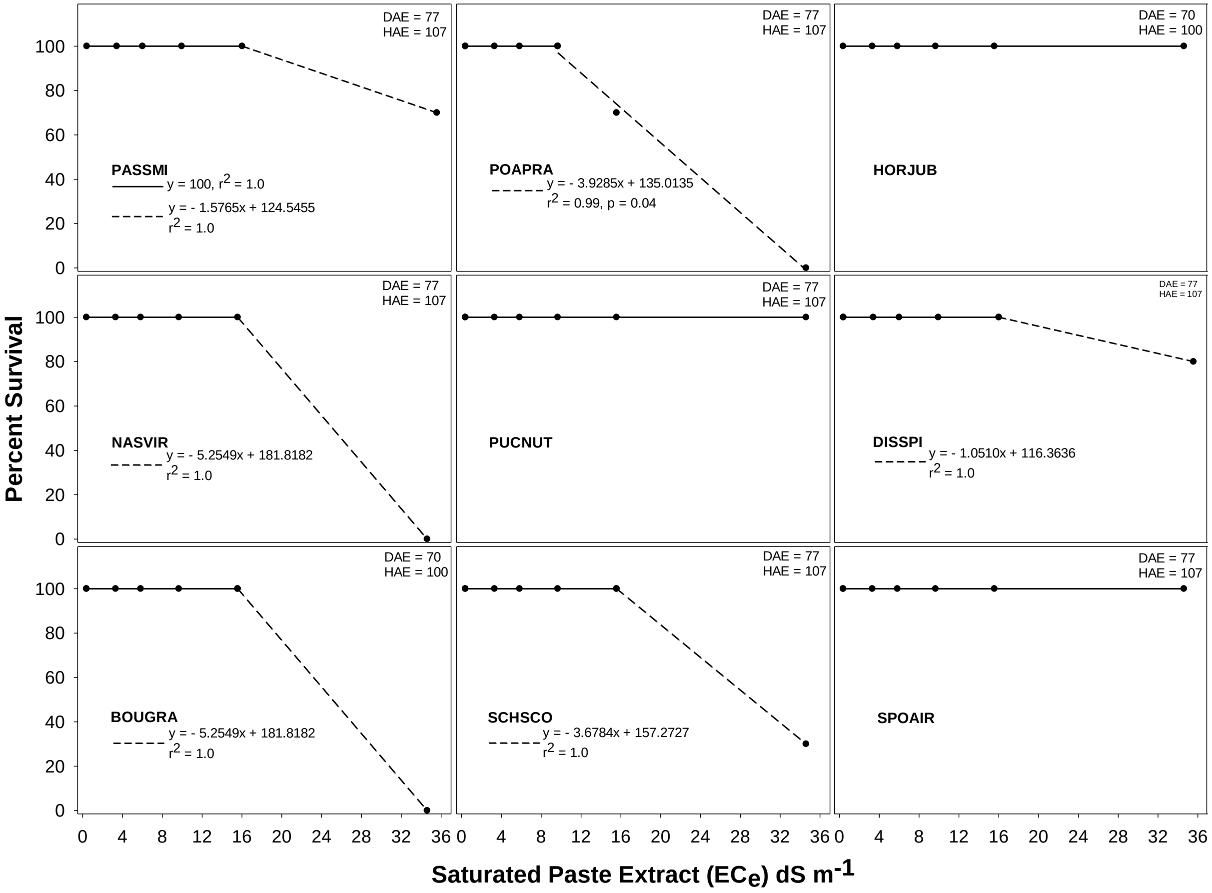

Figure 1: Percent survival of seedlings on an EC_e gradient with piecewise-linear regression models, r^2, pvalue, brine application days after emergence (DAE), and days harvested after emergence (HAE); plants starting from the upper left-hand corner are *Pascopyrum smithii* (PASSMI), *Poa pratensis* (POAPRA), *Hordeum jubatum* (HORJUB), *Nassella viridula* (NASVIR), *Puccinellia nuttalliana* (PUCNUT), *Distichlis spicata* (DISSPI), *Bouteloua gracilis* (BOUGRA), *Schizachyrium scoparium* (SCHSCO), and *Sporobolus airoides* (SPOAIR).

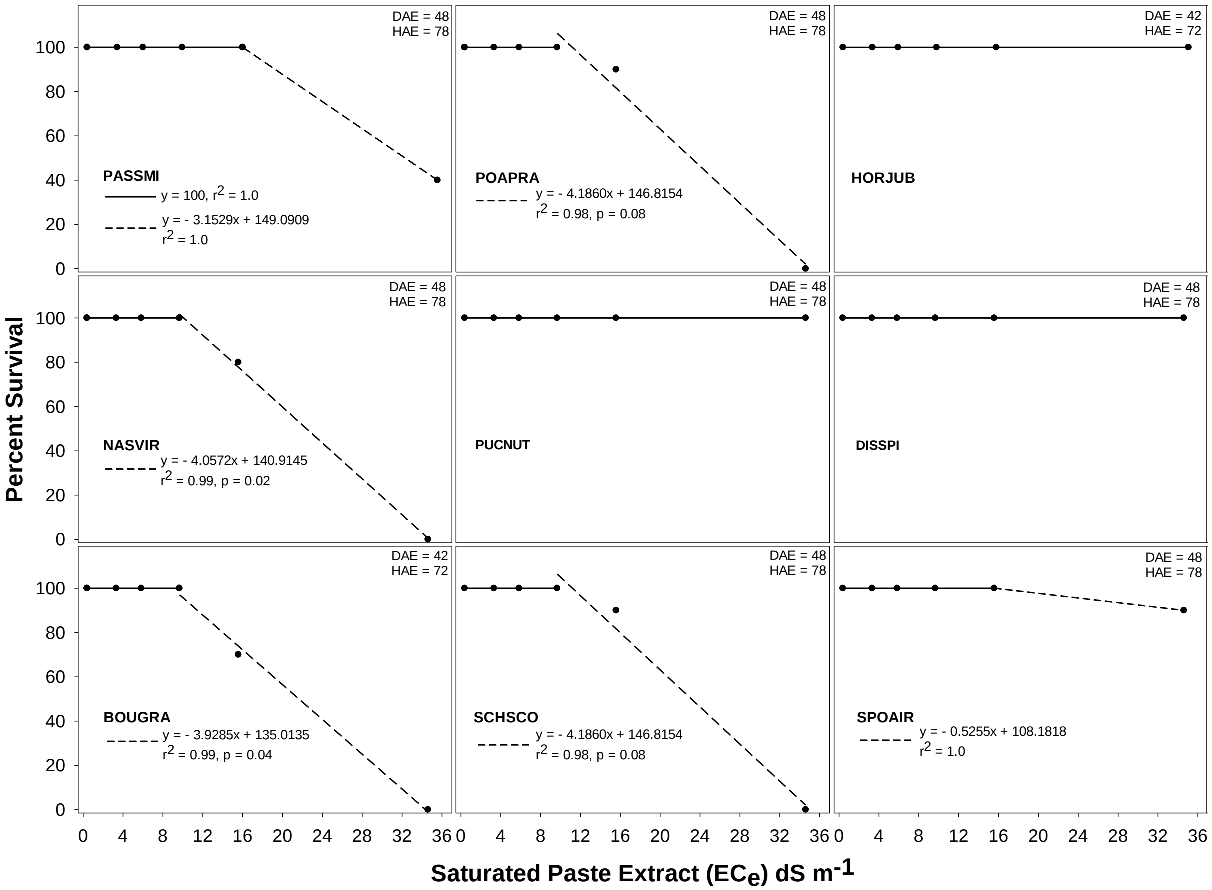

Figure 2: Percent survival of late vegetative — pre-boot plants on an EC_e gradient with piecewise-linear regression models, r^2, pvalue, brine application days after emergence (DAE), and days harvested after emergence (HAE); plants starting from the upper left-hand corner are PASSMI, POAPRA, HORJUB, NASVIR, PUCNUT, DISSPI, BOUGRA, SCHSCO, and SPOAIR.

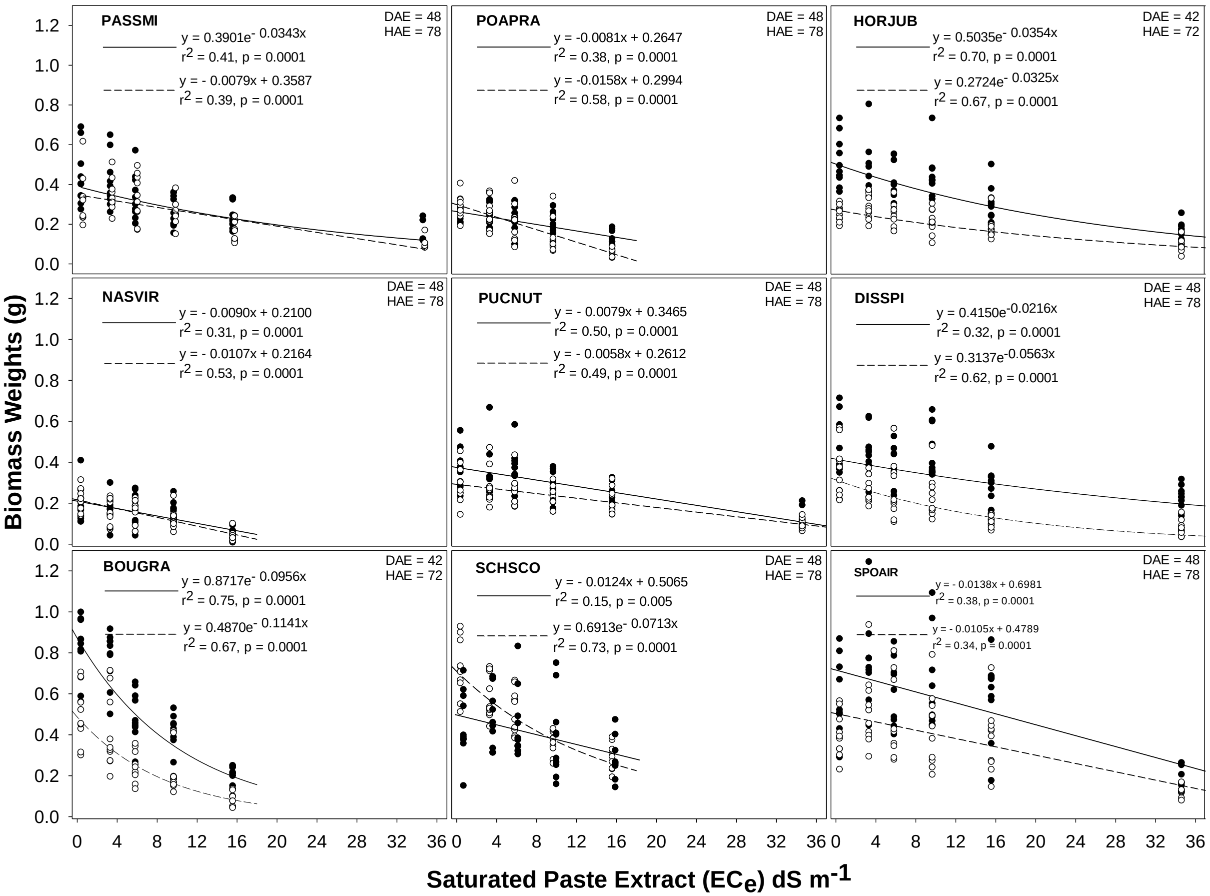

Figure 3: Above (closed circles & solid line) and belowground (open circles & dashed line) biomass weights of seedlings on an EC_e gradient with regression model equations, r^2, pvalue, brine application days after emergence (DAE), and days harvested after emergence (HAE); plants starting from upper left-hand corner are PASSMI, POAPRA, HORJUB, NASVIR, PUCNUT, DISSPI, BOUGRA, SCHSCO, and SPOAIR.

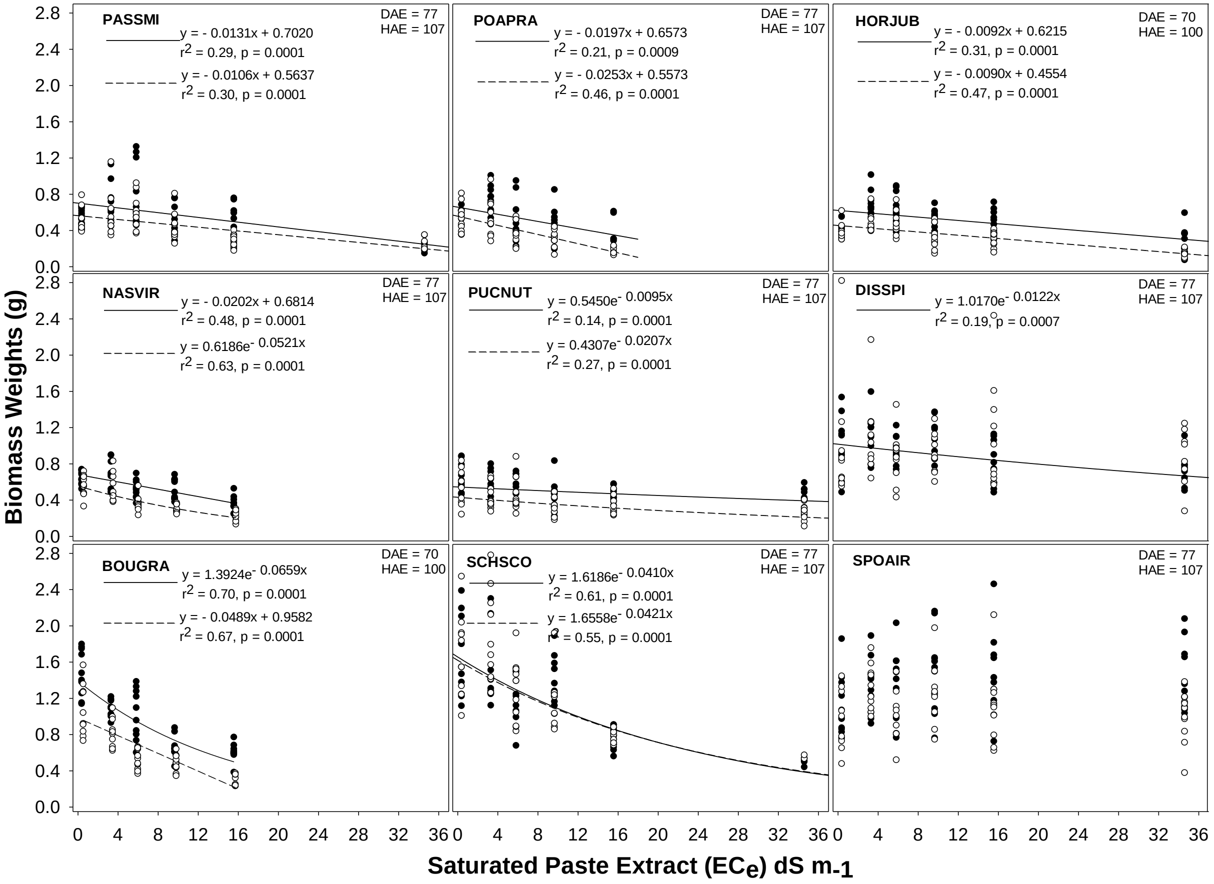

Figure 4: Above (closed circles) and belowground (open circles) biomass weights of late vegetative — pre-boot plants on an ECe gradient with linear and exponential decay regression equation , r^2, pvalue, brine application days after emergence (DAE), and days harvested after emergence (HAE); plants starting from upper left-hand corner are PASSMI, POAPRA, HORJUB, NASVIR, PUCNUT, DISSPI, BOUGRA, SCHSCO, and SPOAIR.

Discussion

The salt ions in the brine limit plants' ability to function properly, requiring immediate human action to reduce ion toxicity and osmotic stress in the soil root zone. This greenhouse study identified potential survival threshold windows (between 9.70 and 18.6 dS m^{-1}) for rangeland plants to determine abiotic levels for revegetation. The five halophytic species (*Pascopyrum smithii*, *Hordeum jubatum*, *Distichlis spicata*, *Puccinellia nuttalliana*, and *Sporobolus airoides*) in this study exhibited higher salt tolerance above 18.6 dS m^{-1} when compared to survival threshold of glycophytic species, with all but two halophytes displaying differences in percent survival at the two growth stages along the soil EC_e gradient. Cool-season grasses *Hordeum jubatum* and *Puccinellia nuttalliana* exhibited 100% survival at the SDLG and LV growth stage along the soil EC_e gradient. The brine thresholds of less salt tolerant plant species (*Poa pratensis*, *Nassella viridula*, *Bouteloua gracilis*, and *Schizachyrium scoparium*) suggest the unlikelihood of natural or artificial reintroduction of these species on salt-affected sites with EC_e above 9.70 dS m^{-1}.

Percent survival of the less salt tolerant plant species, *Bouteloua gracilis*, *Nassella viridula*, and *Schizachyrium scoparium*, increased at the LV growth stage. The observed differences between percent survival and biomass reduction of NMGP species at the two growth stages are likely a result of increased ion transport and storage of salt ions in leaf vacuoles (Munns & Tester 2008). The results of this experiment were similar to other studies that found seedlings were sensitive to increases in soil salinity than at older growth stages (Chartzoulakis & Klapaki 2000; Heo et al. 2007). Mature plants are generally better at regulating water intake and loss, as well as partitioning Na^+ ions to prevent salt accumulation in the cytoplasm and cell wall (Munns 2002; Munné-Bosch and Alegre 2004; Munns 2005). The majority of species observed in this experiment with the exception of *Poa pratensis*, exhibited increased salt tolerance at the older growth stage. *Poa pratensis* responded the same to soil salinity levels regardless of growth stage, which may indicate similar physiological restrictions occur at both stages. Along with physiological traits, salt tolerance is also associated with grass morphology as it relates to water uptake and plant establishment processes (De Jong 1978; Schwarz & Redmann 1990; Flowers et al. 2010).

Cool-season (C_3) grasses tend to dominate the plant community during the early spring and late fall portion of the growing season in the NMGP when lower temperatures and evaporation rates occur (Barnes et al. 1983). The survival of these halophytes in salt-rich environments may be due to their ability to cease tiller development in late-May before salts rise to the soil surface to meet the evaporative demand of the soil surface, which can inhibit plant growth (Singh et al. 1983; Schwarz & Redmann 1980; Tarasoff et al 2007b). The initial development of roots and access to valuable plant resources can potentially make them more competitive and less sensitive to salinity than warm season grasses (Mahall & Park 1976; Tiku 1976). Cool-season halophytic grasses in this experiment were *Hordeum jubatum*, *Puccinellia nuttalliana*, and *Pascopyrum smithii*. *Pascopyrum smithii* was the least salt tolerant of the three with a survival threshold between 18.6 and 34.6 dS m^{-1}.

Pascopyrum smithii is the most widely used native halophyte in seed mixes for reclamation in western rangelands (Richards et al. 1998). The species' survival and biomass production were more affected at the SDLG growth stage than at the LV growth stage in this experiment, which may pose long-term problems for plant establishment and recruitment if salinity levels remain high (> 9.70 dsm^{-1}). Differences between SDLG and LV percent survival and productivity may depend upon osmotic adjustment of cell-sap molarities to maintain turgor and cell volume during salt stress (Bernstein 1961; Munns 1988), and selective uptake and transport of potassium (K^+) ions over sodium (Na^+) ions (Apse & Blumwald 2007; Guo et al. 2015) at different growth stages. Additionally, *Pascopyrum smithii* may lose the ability to selectively uptake K^+ over Na^+ ions and transport them into plant tissues at high salinity levels (Munns & Tester 2008; Guo et al. 2015), such as concentrations (EC_e 18.6 and 34.6 dS m^{-1}) tested in this experiment.

Short-lived halophytic grasses circumvent osmotic stress to some extent by fast tracking their life cycle to avoid costly plant inputs. *Hordeum jubatum*, ruderal halophyte, exhibited 100% survival at both growth stages up to EC_e of 34.6 dS m^{-1}. *Hordeum jubatum*, is successful in saline environments because it can selectively uptake potassium (K^+) and calcium (Ca^{2+}) ions to young plant shoots, while reducing Na^+ and Cl^- uptake and storing salt (NaCl) ions into above and belowground vacuoles (Badger & Ungar 1990; Keiffer & Ungar 2001; Keiffer & Ungar 2002). This mechanism is beneficial for temporarily reducing soil salinity in the growth medium to facilitate the reintroduction of less salt tolerant plant species as soil salinity decreases (Keiffer & Ungar 2001; Keiffer & Ungar 2002). However, harvesting aboveground biomass is necessary to permanently remove salt ions stored in leaf vacuoles and prevent long-term salt ion cycling in the soil matrix. Biomass production of seedlings were more sensitive to soil salinity than at the older growth stage and is comparable to observed field conditions (Cords 1960; Badger & Ungar 1989). *Hordeum jubatum* compensates for this failure by maturing early, which allow brittle heads to break away from the rachis and disperse seeds across the landscape (Cords 1960; Best et al. 1978). These seeds then germinate shortly after dispersal or during periods of reduced soil salinity to yield monotypic stands (90 to 100%) of *Hordeum jubatum* on salt-rich areas (Badger & Ungar 1989; Badger & Ungar 1994). Although *Hordeum jubatum* can readily inhabit these types of habitats, it is a poor competitor with perennial, deep-rooted plants at lower salinities (Cords 1960; Wilson 1967: Best et al. 1978). The results of this greenhouse experiment display the potential use of *Hordeum jubatum* as a field indicator species to identify problematic salt-affected areas on remediated brine spill sites.

Puccinellia nuttalliana is a perennial bunchgrass that provides ground cover, forage resources, and wildlife habitat once established (Liu & Coulman 2015). Similar to *Hordeum jubatum*, *Puccinellia nuttalliana* was unaffected at the higher EC treatments, making it a more desirable and competitive species as compared to shallow rooted, short-lived *Hordeum jubatum*. However, the specific salt tolerant mechanism of *Puccinellia nuttalliana* is unknown (Tarasoff et al. 2007a; Tarasoff et al. 2010), and reportedly does not store salt ions in above or belowground plant parts (Tarasoff et al. 2007a; Tarasoff et al. 2010). *Puccinellia nuttalliana* may use salt-avoidance strategies, such as delaying germination at high salinities, excluding salt ion uptake at the root interface, and ceasing tiller development before salt-laden water rises when the soil becomes dry and moves towards the soil surface (Schwarz & Redmann 1990; Tarasoff et al. 2007b). The high salt tolerance of *Puccinellia nuttalliana* at early growth stages, as indicated by this greenhouse experiment, may enable this plant to establish in salt-rich areas and take advantage of plant resources (e.g., water, nutrients, light, and space) that glycophytes are unable to access (Macke & Ungar 1971; Tarasoff et al. 2007; Gilbert & Fraser 2013). Although we did not assess the competitive ability of *Puccinellia nuttalliana* in this experiment, this plant is a deep-rooted, perennial halophyte that can stabilize soil to minimize wind and water erosion on salt-affected areas (Kenkel et al. 1991; Gilbert & Fraser 2013).

Warm-season (C_4) grasses, to some extent, are salt tolerant in order to survive in semi-arid to arid climates where drought and salinity often coincide (Bromham 2015). These two abiotic stressors behave similarly by activating and regulating different stress response mechanisms to cope with a reduction in total soil water potential energy in the growing medium (Wang et al. 2003; Hu & Schmidhalter 2005). Warm-season grasses differ from cool-season grasses in that they can better regulate water intake and loss during periods of drought and salt stress (Barnes et al. 1983; Schwarz & Redmann 1990; De Jong 1978). Warm-season halophytic grasses in this experiment were *Distichlis spicata* and *Sporobolus airoides*, each with a detected brine threshold between 18.6 and 34.6 dS m^{-1} at the LV and SDLG, respectively.

Distichlis spicata and *Sporobolus airoides* both belong to the Chloridoideae subfamily and are salt accumulating halophytes (Marcum 1999). Salt accumulating halophytes compartmentalize salt ions in leaf vacuoles, utilizing specialized glands to excrete salt (Na^+ & Cl^-) ions to outside the plant (Hansen et al. 1976; Marcum 1999). Salt accumulating halophytes reportedly recover faster from high concentrations of salts in growing medium than salt-excluding halophytes that tend to grow better at lower soil EC_e levels (Greenway 1968). *Distichlis spicata* was slightly more salt tolerant at the LV growth stage than at the seedling stage, and was the only species to display this relationship in our study. Increased mortality at the LV growth stage is likely associated with the divergence of resource allocation to support reproductive structures and lower salt-accumulation at high salinity levels (Marcum 1999). *Sporobolus airoides* differed from *Distichlis spicata* in having a lower brine threshold at the SDLG growth stage (between 18.6 and 34.6 dS m^{-1}) and no response at the LV stage (> 34.6 dS m^{-1}) and vice versa. *Sporobolus airoides* and *Distichlis spicata* can accumulate and compartmentalize brine salts (Na^+ & Cl^-) in plant tissues (Hansen et al. 1976; Marcum 1999), allowing for the harvesting of aboveground plant growth and permanently reducing salt ions in the plant root zone.

Management Strategies

The native halophytes examined in this project are viable options for reclaiming salt-affected rangelands, while providing food and cover to wildlife species and forage for livestock. *Distichlis spicata* and *Pascopyrum smithii* provide high crude protein (CP) content (CP; 15.0 and 18.5%, respectively) during early spring when high quality forage is necessary for maintenance of lactating mammals (Hart et al. 1963; Hansen et al. 1976). In addition to forage value, *Sporobolus airoides* grows tall and dense, providing shelter and camouflage for wildlife species (Hickey & Springfield 1996). These native halophytes are preferable over non-native halophytes because they facilitate the reintroduction of less salt tolerant grasses and forbs to increase biodiversity and are less likely to create monotypic communities. Dominance of non-native halophytes, such as *Agropyron cristatum* (L.) Gaertn., and *Bassia scoparia* (L.) A.J. Scott, on salt-affected soils prevent ecosystem recovery and delay the bond release process for remediated brine spill sites. Reclaiming recently remediated brine spill sites with native halophytes may increase the success rate of reseeding applications and possibly reduce exotic halophyte establishment.

Conclusions

Evaluation of native halophytic plant species through greenhouse and field studies creates new science for improving remediation techniques on land affected by natural and anthropogenic surface salinity. The halophytes species in this greenhouse experiment exhibited a brine threshold between 18.6 and 34.6 dS m^{-1} EC_e, which was higher than the brine threshold of glycophyte species (9.70 and 18.6 dS m^{-1} EC_e). *Hordeum jubatum* and *Puccinellia nuttalliana* exhibited 100% survival up to 34.6 dS m^{-1} at both SDLG and LV growth stages, indicating a higher brine threshold. SDLG percent survival and biomass production was lower than the LV growth stage, with increasing soil salinity. Since plant mortality and biomass production declined with plant age, it may be beneficial to transplant seedlings to promote plant establishment and growth during periods of increased soil moisture sooner, before the soil dried out, to circumvent scorching of newly established seedlings when salt-laden water rises from deeper to upper soil horizons. Unfortunately, many of the native halophytic species discussed in this paper are not widely used in oil and gas reclamation seed mixes. *Pascopyrum smithii* is the most popular halophyte species for revegetating western rangelands due to its availability and moderate price (Richards et al. 1998). The results of this paper provide an opportunity for oil and gas personnel to diversify their native seed selection by selecting native halophytes (e.g., *Distichlis spicata*, *Puccinellia nuttalliana* and *Sporobolus airoides*) to increase plant establishment and future recruitment on salt-affected sites. *Hordeum jubatum* is a ruderal halophyte that is likely to revegetate salt-affected sites without artificial assistance and replaced by perennial, deep-rooted species when EC_e levels decline to acceptable levels for glycophytes. Selection of halophytes with different salt tolerant mechanisms and life histories are important for ensuring permanent vegetation cover on salt-affected sites.

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APPENDIX E

EVALUATION OF SOIL TREATMENT TECHNIQUES ON REMEDIATED BRINE WATER SPILL SITES IN SEMI-ARID RANGELANDS

EVALUATION OF SOIL TREATMENT TECHNIQUES ON REMEDIATED BRINE WATER SPILL SITES IN SEMI-ARID RANGELANDS

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Abstract

Oil-produced water (i.e. brine) is a waste product of oil and gas extraction that can cause severe changes to soil chemistry and plant communities when discharged onto the soil surface. Brine spill remediation through topsoil excavation (*ex situ*) or the addition of chemical amendments (*in situ*) aims to remove or minimize the abiotic stressor to levels suitable for plant growth. We quantified residual brine salts and plant establishment on 10 chemical amendment and 11 topsoil excavation sites in semi-arid rangelands of western North Dakota. Paired reference and remediated sites had similar soil texture and landscape position. We hypothesized no difference in soil and plant parameters between remediation techniques. Results concluded electrical conductivity (EC_e) was not different ($p > 0.05$) between remediation treatments for all three depths. Overall plant productivity was different ($p \leq 0.05$) between remediated and reference sites, but not between remediation techniques ($p > 0.05$). Remediation techniques successfully lowered EC_e to facilitate natural and assisted revegetation. Species composition and diversity on remediated sites were different ($p \leq 0.05$) between remediated and reference sites, indicating that remediated sites are undergoing succession and not yet similar to neighboring plant communities. Based on our findings, chemical amendments are the preferred remediation technique on small brine spill sites because they are less invasive and a more sustainable option than topsoil excavation.

Introduction

Global oil and gas exploration and extraction contributes to environmental degradation (Asif and Muneer 2007), loss of ecosystem services (Allred et al. 2015), and the development of novel rangeland ecosystems when abiotic and biotic properties are altered (Hobbs et al. 2006; Hobbs et al. 2009). Oil and gas development increase human access to once remote areas (Finer et al. 2008), and weaken the structure and function of ecosystems by introducing a suite of new species (i.e. exotics; Hobbs and Huenneke 1992). While surface disturbances from oil and gas development disrupt the biotic component of ecosystems, contaminants from these human-induced activities change the abiotic properties of soil, making it increasingly difficult for plants to survive in these areas (Murphy et al. 1988; Keiffer and Ungar 2001). Discharges of oil-produced water (i.e. brine) and hydrocarbons can contain salt concentrations that kill vegetation and change plant community assemblages. Brine contaminated land, if left untreated, can create novel ecosystems that put additional pressure on intact remnant communities, requiring human-intervention to lessen the negative impacts caused by surface contamination and disturbance.

Oil-produced water (i.e. brine) spills are arguably the most environmentally destructive contaminant and controversial aspect of the oil and gas extraction process (Jager et al. 2005; Aschenbach and Kindscher 2006). Brine can contain up to 90% NaCl salts (McMillion 1965; Merrill et al. 1990) and can induce soil electrical conductivities (EC) much higher ($\leq$ 200 dS m^{-1}) than natural salinity (Jong 1982; Keiffer & Ungar 2002). Spills may occur when there is a tank battery overflow, pipeline leak, or migration of salts from a reserve pit (Murphy et al. 1988; Sublette et al. 2007). Accidental or deliberate releases of brine can have long lasting impacts on soil and vegetation parameters.

Sodium from spills weaken soil aggregate stability by dispersing clay particles and plugging soil pores and thus reducing hydraulic conductivity (Jager et al. 2005; Leskiw et al. 2012). Releases of brine onto the soil surface overwhelm a plants' ability to cope with large quantities of salt at one discrete time, leading to ion toxicity (Munns and Termaat 1986; Halvorson and Lang 1989; Munns 2002). Brine salts also impede future plant establishment and recruitment by decreasing the soil water osmotic potential (Harris et al. 2005; Jager et al. 2005; Leskiw et al. 2012), requiring plants to expend more energy to extract water and nutrients from the soil matrix.

The severity of brine spills depends on the environment in which they occur. Brine in semi-arid to arid climates ($\leq$ 25 cm year $^{-1}$) tend to have long-term impacts due to low moisture and soil leaching (Keiffer and Ungar 2001; Keiffer and Ungar 2002). Increases in soil moisture during months with ample precipitation lead to vertical and horizontal expansion of brine salts (brine plumes; Murphy et al. 1988), which can resurface during dry months when leached soil water rises to the soil surface via capillary action to meet atmospheric demand (Thimm 1990). Natural processes do not lessen the negative effects of brine salts over a reasonable management timescale. A legacy non-remediated brine spill sites (> 60 year-old) in western North Dakota had a saturated paste electrical conductivity (EC_e) value of 126 dS m^{-1} (Klaustermeier et al. 2016), which is 30 times higher than what the USDA classifies as saline-sodic soils (EC_e of 4 dSm^{-1}; USDA 1954). Brine spill remediation through soil treatment techniques such as topsoil excavation (*ex situ*) and leaching with calcium amendments (*in situ*) are used to ameliorate site conditions and increase the success rate of both natural and assisted plant reintroduction towards a predefined state.

Traditional remediation techniques aim to reduce adverse effects on human health or ecological risks associated with brine contamination. Topsoil excavation (*ex situ*) removes the impacted soil to the depth of infiltration and introduces replacement soil. This method permanently reduces the quantity of brine salts but requires a source for the replacement soil. The most common *in situ* method involves divalent (Ca^{2+}) based salts, primarily gypsum ($CaSO_4^{2-}$) and calcium chloride ($CaCl_2$), to displace monovalent sodium (Na^+) ions from soil cation exchange sites and move them from upper to lower soil depths (Jong 1982; Halvorson and Lang 1989; Taylor et al. 199). Differences in soil and vegetation parameters between remediation techniques may play an important role in determining plant community assemblages long after completion of remediation.

Brine spills can create novel ecosystems when remediation techniques do not return soil and plant parameters to pre-spill conditions. Chemical amendments are often preferred over topsoil excavation as they minimize the disruption of the soil structure when reducing soil EC_e levels, allowing plant roots to penetrate deeper into the soil profile to extract water and nutrients. However, the application of this technique indiscriminately discharges desirable plant nutrients below the plant root zone where they are inaccessible to plant roots, thus reducing soil fertility and reducing plants ability to propagate these sites. Topsoil excavation invokes a different strategy by rapidly reducing soil contaminants all at once. However, replacement soil has less soil structure due to the multiple disturbances needed to collect, haul, and replace soil. Soil with less structure will influence plant composition and abundance by restricting plant roots from entering soil pores that are smaller than their diameter (Wiersum, 1957), resulting in slower root growth (Pardo et al. 2000; Bronick and Lal 2005). The loss of plant productivity can lead to patches of bare soil that are susceptible to erosional processes, reducing soil fertility and preventing plant establishment and recruitment. Given the variability in performance between remediation techniques, an assessment is necessary to determine how each remediation technique affects soil and plant parameters under a semi-arid climate.

Current remediation practices aim towards reducing the amount of time, money, and energy spent at each contaminated site. However, “fast and effective” do not always complement each other, and sites may require additional follow-up treatments to finalize the remediation process. A formal assessment of these two traditional remediation techniques (leaching with chemical amendments and topsoil excavation) across a variety of ecological sites is necessary to determine which method is more appropriate for the environmental conditions in semi-arid rangelands. The objective of this field study was to compare the efficacy of the two soil remediation techniques (*in situ* & *ex situ*) by evaluating residual brine salts and quantifying plant establishment on remediated brine spill sites on semi-arid rangelands. We hypothesize no difference in soil and plant parameters between reference sites and respective remediation techniques.

Materials and Methods

The study area was located on the Little Missouri National Grasslands (LMNG) in western North Dakota, USA. The LMNG is primarily managed for cattle grazing and wildlife habitat (Reeves et al. 2006), but is experiencing an increase in oil and gas development in the last decade (NDIC-OGD 2016). The dominant soil types in this area include well-drained loams, clay loams, and sandy loams (Setter and Lym 2013). Climate is continental and semi-arid, with mean temperatures ranging from -15 °C in winter to 23 °C during the growing season (April-September), and a mean annual precipitation and potential evaporation of 425 and 3.81 mm, respectively (NDAWN 2016), with 70% of precipitation occurring between May and September.

Historic natural vegetation includes western wheatgrass (*Pascopyrum smithii* (Rydb.) Á. Löve), blue grama (*Bouteloua gracilis* (Willd. ex Kunth) Lag. ex Griffiths), needle and thread (*Hesperostipa comata* (Trin. & Rupr.) Barkworth subsp. *comata*), green needlegrass (*Nassella viridula* (Trin.) Barkworth), prairie junegrass (*Koeleria macrantha* (Ledeb.) Schult.), and threadleaf sedge (*Carex filifolia* Nutt.) (Reeves et al. 2006; Setter and Lym 2013). Plant nomenclature follows the USDA Plants Database (USDA 2016).

We sampled 10 chemical amendment and 11 topsoil excavation sites in the summer of 2015 across seven ecological sites. Sites varied by time since remediation (2007-2014), size (14 × 14 m^2 to 45 × 45 m^2), and amount of brine split (3 to 690 bbls; Appendix A). We used a paired-plot design, paring each remediated brine spill site with a nearby reference site similar in soil texture and landscape position. We also compared our reference sites to random sites located within the LMNG to determine if our reference sites represent the current state of the grasslands across sampled ecological sites. These random sites are a more accurate representation of the plant community and productivity of the LMNG because data collection occurred at a minimum distance of 200 m from anthropogenic structures, such as fences, roads, and water sources.

Since brine spills are irregular in size, the number of data frames collected from each site reflected the size of the remediated brine spill area (250 frames/ha^{-1}). Soil samples were collected at three depths (0-15, 15-30, and 30-60 cm) along two intersecting transects at each site. We analyzed subsamples of remediated and reference sites for topsoil excavation sites at the 0-15 cm depth for soil texture using the pipette method (Black 1965).

Preparation of soil samples followed guidelines for 1:1 soil-to-water suspensions ($EC_{1:1}$) as described in Handbook 60 of the United States Department of Agriculture (USDA 1954). The $EC_{1:1}$ were then converted to saturated paste extract (EC_e) values as described by Klaustermeier et al. (2016). We converted our $EC_{1:1}$ to EC_e because EC_e naturally simulates saturated soil conditions to predict plants' response to soil salinity (Zhang et al. 2005). Statistical analysis for soil data included one-tailed t-tests at a specified value of zero to compare the mean differences in EC_e between reference and remediated sites and two-tailed t-tests between remediation techniques.

Visual estimation of plant cover occurred in 1×1 m frame using a modified cover class method (0-1%, 1-2%, 2-5%, 5-10%, 10-20%, 20-30%, 30-40%, 40-50%, 50-60%, 60-70%, 70-80%, 80-90%, 90-95%, 95-98%, 98-100%) (Daubenmire 1959) and using the midpoint values for each class for statistical analysis. We harvested and separated plants into native and non-native life form groups (forb, grass, and shrub) in the 1×1 m frame and oven dried (48 °C) them to a constant weight. Statistical analysis included two-tailed t-tests to compare the mean difference between reference and remediated sites, and between remediation techniques to analyze biomass and ground cover parameters. Ground cover parameters included visual estimation of basal and canopy cover of bare ground and litter (plant residue and man placed plant materials). Data analysis included subtracting the mean differences between reference and remediated sites in the same direction each time. Mean differences of values are either positive or negative to reflect changes in plant productivity among ecological sites. We compared plant productivity of paired reference sites with data collected from random sites in the summer of 2013 and 2014 on the LMNG using similar ecological sites. Sites were analyzed using Nonmetric Multidimensional Scaling (NMS) ordination in PC-ORD® vs. 6.0 multivariate statistical software program.

The Relative Sørensen Dissimilarity Index was used to determine contrast differences in species proportions between remediated reference sites (McCune and Grace 2002). We also used

PC-ORD to compare differences between reference and remediated sites using the PerMANOVA function and to compute diversity indices. Statistical analysis of diversity indices and Sørensen dissimilarity index include one-tailed t-tests at a specific value of zero and two-tailed t-tests.

Results

The mean soil EC_e difference was not different ($P \geq 0.05$) between remediation techniques (Figure 5) for all three depths. Soil EC_e had the lowest values for both remediation techniques at the 0-15 cm depth, with chemical amendment sites (-2.96 ± 1.07 dS m^{-1}) having a slightly higher EC_e than topsoil excavation sites (-2.08 ± 0.69 dS m^{-1}). Electrical conductivity at the 15-30 cm depth for chemical amendments and topsoil excavation sites were -4.14 ± 1.42 and -2.76 ± 1.88 dS m^{-1}, respectively. The highest soil EC_e for both chemical amendments (-4.45 ± 1.52 dS m^{-1}) and topsoil excavation sites (-2.64 ± 2.25 dS m^{-1}) occurred at the 30-60 cm depth. The soil EC_e values were different ($P < 0.05$) between remediated and reference sites for all three depths at the specified value of zero.

The mean percent difference for bare ground was different ($P < 0.05$) between chemical amendment (-15.6 ± 5.99%) and topsoil excavation sites (-55.0 ± 7.18%), and between remediated and reference sites (Figure 6). Chemical amendments (18.3 ± 6.19%) had less bare ground than topsoil excavation (58.7 ± 6.67%) sites, and was more similar to reference sites (2.68 ± 0.91 and 3.62 ± 1.45%, respectively). Litter was not different ($P \geq 0.05$) between chemical amendment sites (-1.77 ± 5.12%) and topsoil excavation sites (8.22 ± 2.54%), but was different ($p < 0.05$) between remediated and reference sites (Figure 6). Litter was higher on chemical amendment (13.0 ± 3.12%) than on topsoil excavation sites (1.54 ± 0.57%), and was more similar to reference sites (11.2 ± 2.61 and 9.75 ± 2.53%).

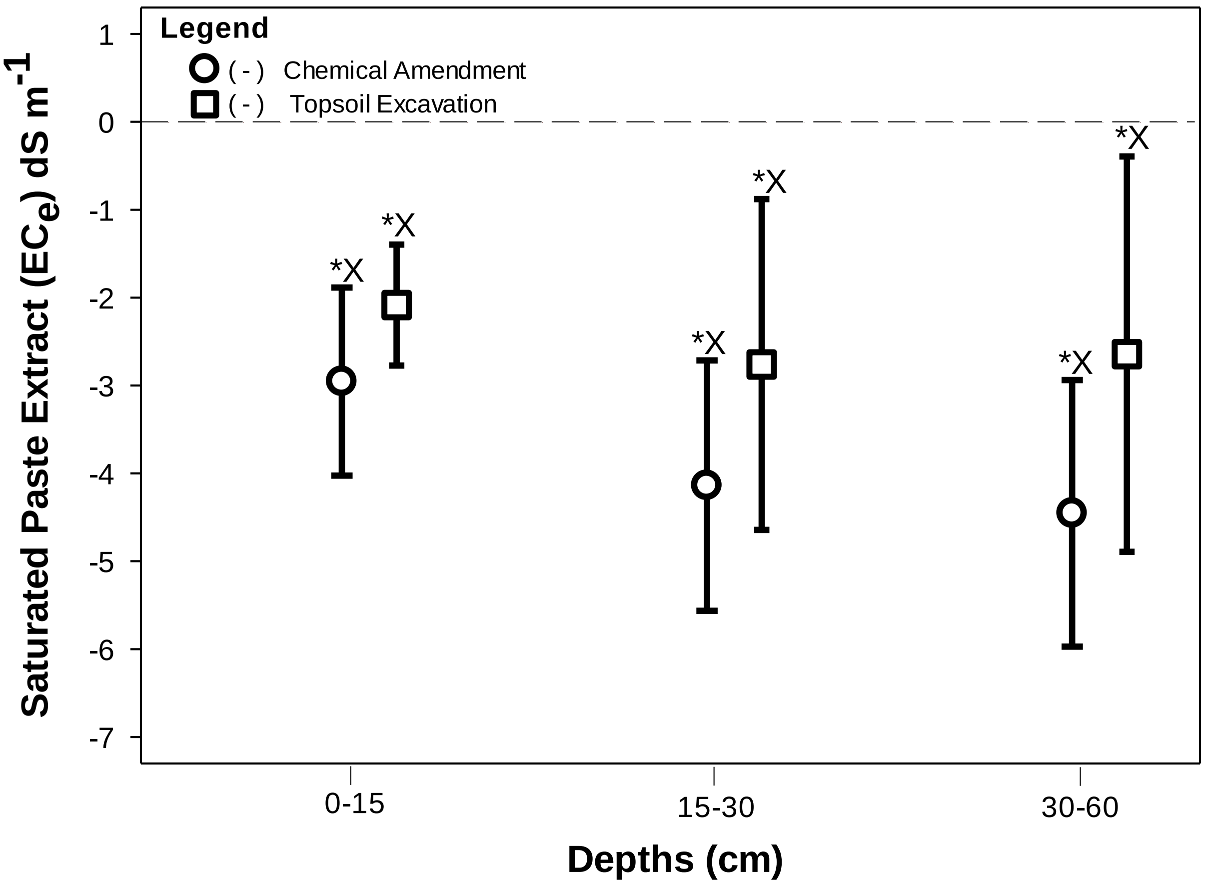

Figure 5: Significant mean difference of soil EC_e between remediated and reference sites at a specified value of zero are indicated by as asterisk (*), and between chemical amendment and topsoil excavation techniques (X's & Y's) at 0-15, 15-30, and 30-60 cm across seven ecological sites on the Little Missouri National Grasslands in western North Dakota.

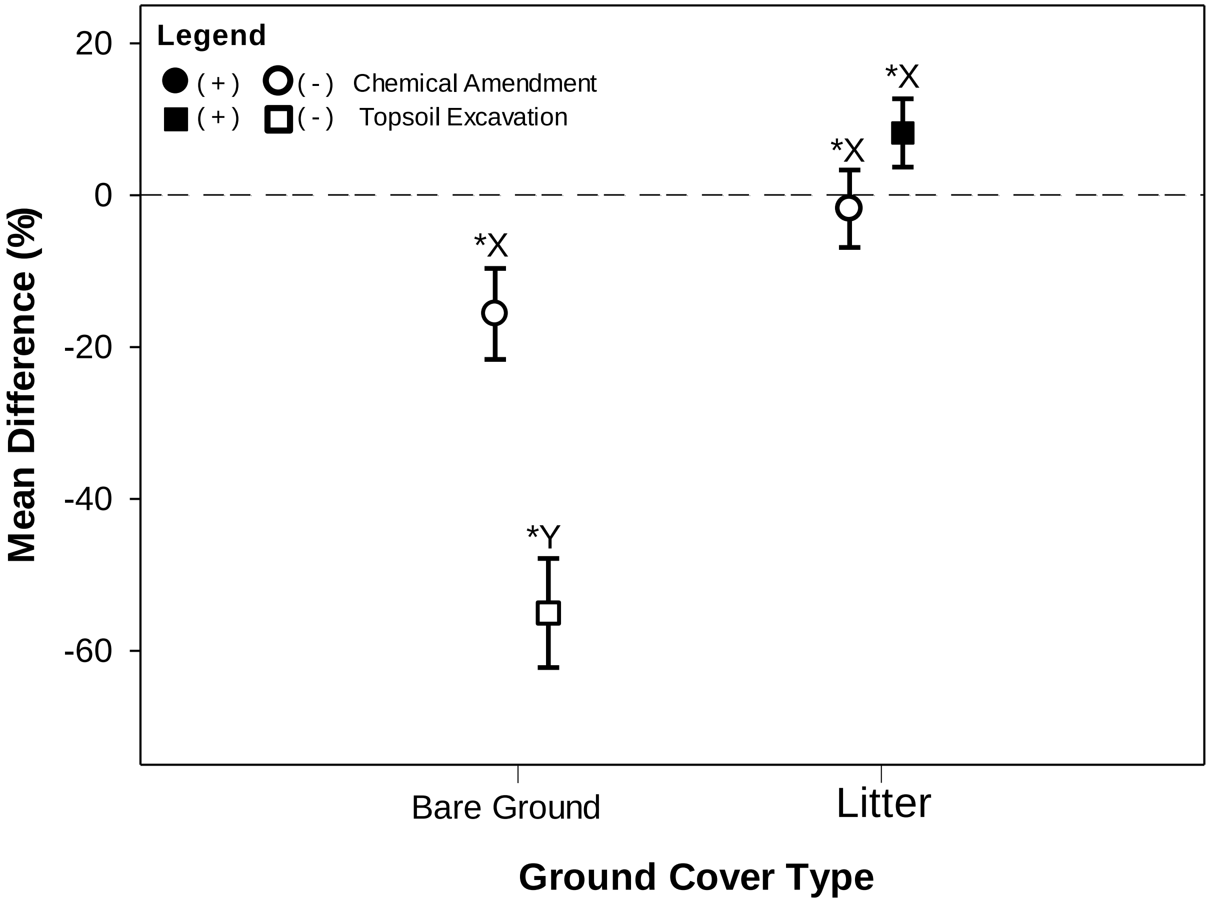

Figure 6: Percent mean difference in basal and canopy cover between remediated and reference sites. Significant differences between remediated and reference sites are indicated by as asterisk (*) and between chemical amendment and topsoil excavation techniques (X's & Y's) for bare ground and litter across seven ecological sites on the Little Missouri National Grasslands in western North Dakota.

Native grass biomass was not different ($P \geq 0.05$) between chemical amendment (2.76 ± 25.5 g) and topsoil excavation sites (54.5 ± 15.1 g), but was different ($P < 0.05$) between remediated and reference sites (Figure 7). Native grass biomass was considerably higher on chemical amendment (63.8 ± 34.6 g) than topsoil excavation (10.0 ± 2.86 g) sites, as compared to reference (60.6 ± 17.0 and 64.5 ± 16.0 g) sites. Exotic grass biomass was not different ($P \geq 0.05$) between chemical amendment (-10.4 ± 21.1 g) and topsoil excavation (20.6 ± 16.5 g) sites, or between remediated and reference sites (Figure 7). Exotic grass biomass on chemical amendment (32.1 ± 14.4 g) and topsoil excavation sites (14.7 ± 6.70 g) were similar to exotic grass biomass on reference sites (19.7 ± 10.0 and 35.3 ± 14.3 g).

Native forb biomass was different ($P < 0.05$) between chemical amendment (7.66 ± 2.24 g) and topsoil excavation sites (-7.65 ± 5.85 g), and between remediated and reference sites (Figure 7). Chemical amendments sites (2.29 ± 0.89 g) had a lower native forb biomass than topsoil excavation sites (13.0 ± 6.12 g), with topsoil excavation sites more closely resembling reference sites (9.08 ± 2.17 and 5.39 ± 1.20 g). Exotic forb biomass was not different ($P \geq 0.05$) between chemical amendment (-29.2 ± 14.8 g) and topsoil excavation sites (-29.5 ± 10.9 g), but was different ($P < 0.05$) between remediated and reference sites (Figure 7). Chemical amendment (32.4 ± 15.6 g) and topsoil excavation sites (29.8 ± 10.9 g) had higher exotic forb biomass as compared to reference sites (3.01 ± 1.57 and 0.31 ± 0.19 g).

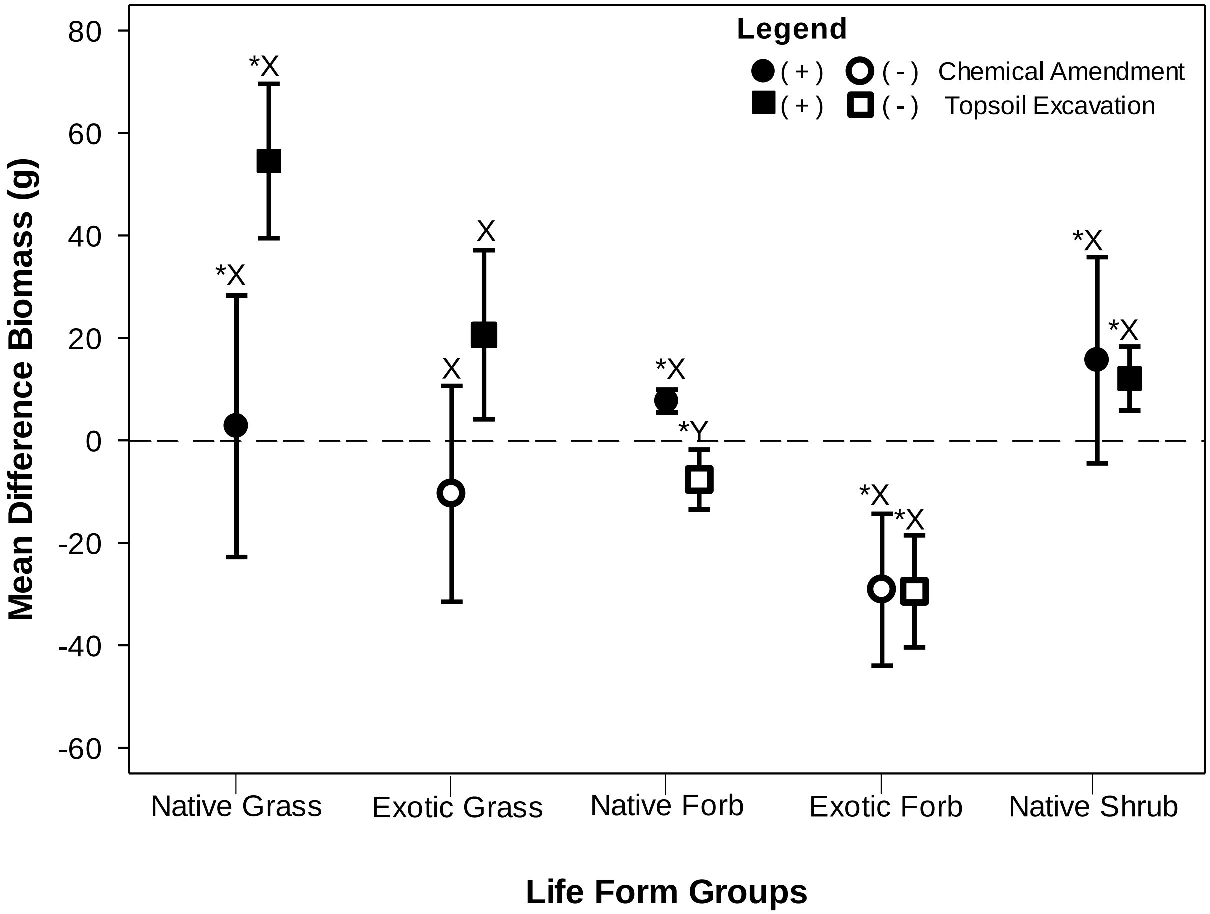

Figure 7: Significant mean differences in biomass between remediated and reference sites are indicated by as asterisk (*), and between chemical amendment and topsoil excavation techniques (X's & Y's) for native grass, exotic grass, native forb, exotic forb, and native shrub across seven ecological sites on the Little Missouri National Grasslands in western North Dakota.

Native shrub biomass was not different ($P \geq 0.05$) between chemical amendment (15.6 ± 20.1 g) and topsoil excavation sites (12.1 ± 6.25 g), but was different ($P < 0.05$) between remediated and reference sites (Figure 7). Chemical amendment sites (18.5 ± 10.1 g) had higher native shrub biomass than topsoil excavation sites (2.15 ± 2.15 g), with chemical amendment sites more closely resembling native shrub biomass of reference sites (31.1 ± 16.8 and 14.2 ± 5.98 g).

We observed 140 species across remediated, reference, and random sites. Species richness did not differ ($P \geq 0.05$) between remediation techniques (6.90 ± 1.52 and 5.55 ± 1.84) (Figure 8). However, species richness was different ($P < 0.05$) between remediated and reference sites at a specified value of zero. Species evenness were not different ($P \geq 0.05$) between remediation techniques, or between remediated and reference sites (Figure 8).

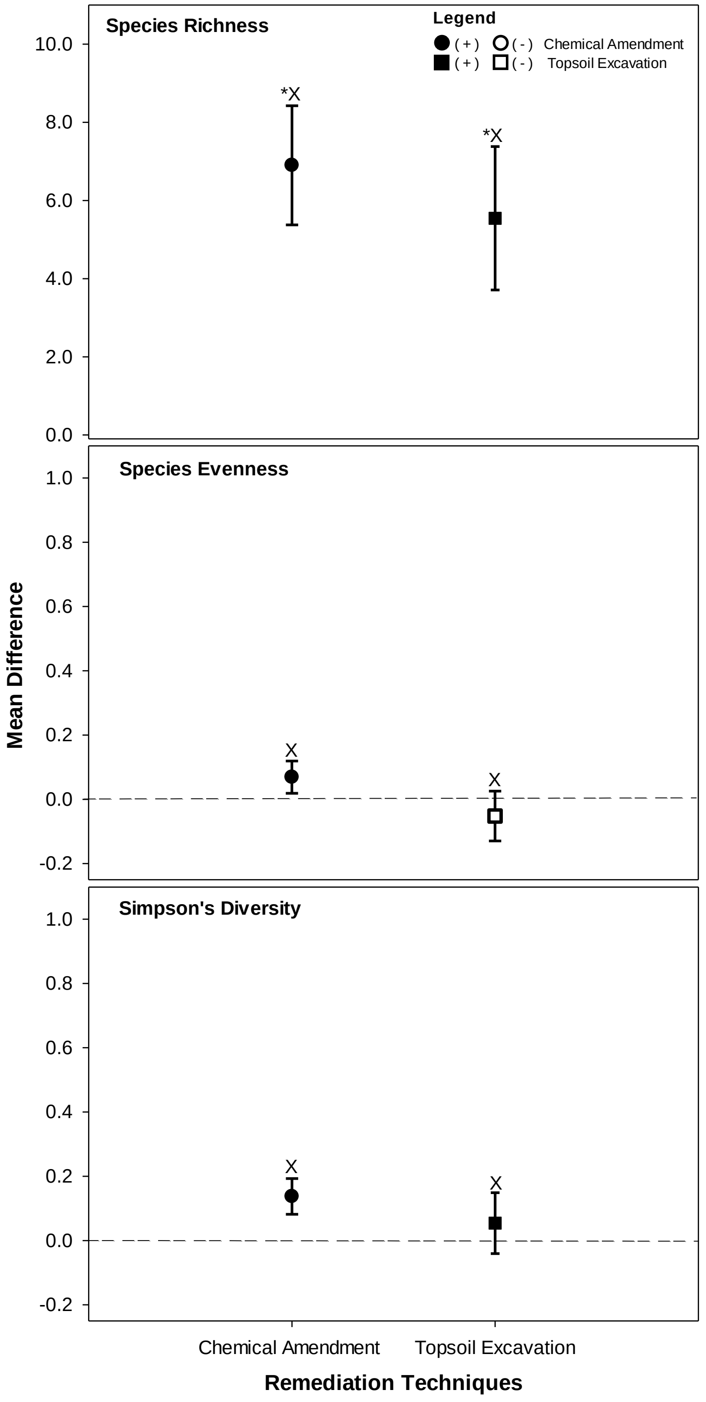

Figure 8: Significant mean differences in diversity indices between remediated and reference sites are indicated by an asterisk (*), and between chemical amendment and topsoil excavation techniques (X's & Y's) for species richness and evenness, and Simpson's diversity across seven ecological sites on the Little Missouri National Grasslands in western North Dakota.

The remediated brine spill sites were different ($P < 0.05$) from the reference sites as indicated by the PerMANOVA (Figure 9). The NMS ordination diagram separates Axis 1 and Axis 2, with Axis 1 corresponding to cover of early successional and exotic species across remediated and reference sites (Figure 9). Axis 1 (25%) represents the majority of variation in the dataset, whereas Axis 2 represents 15% and Axis 3 (not shown) represents 11% of the variation in the dataset. The three axes explain 51% of the total variation with a final stress of 14. Nineteen reference sites were located on the left side of the ordination axis, correlating with native grass species such as blue grama, green needlegrass, and prairie junegrass as well as the majority of native forb species. Nine remediated sites were located on the right side of the ordination axis, correlating with ruderal and exotic plant species, such as such as field pennycress (*Thlaspi arvense* L.), annual sunflower (*Helianthus annuus* L.), wormwood (*Artemisia absinthium* L.), and kochia (*Bassia scoparia* (L.) A.J. Scott). The middle of the ordination where reference (one site) and remediated (eight sites) sites overlap correlated with salt tolerant plant species (e.g. western wheatgrass, foxtail barely (*Hordeum jubatum* L.), crested wheatgrass (*Agropyron cristatum* (L.) Gaertn). Percent dissimilarity was not different ($P \geq 0.05$) between chemical amendment (0.76 ± 0.08 %) and topsoil excavation sites (0.87 ± 0.04 %) (Figure 10).

The reference sites were not different ($P \geq 0.05$) from the random sites as indicated by the PerMANOVA (Figure 11). Axis 1 (29%) and Axis 2 (20%) explained almost 50% of the variation of the dataset, with early successional and exotic species corresponding to Axis 1 (Figure 11). The two dimensional solution comprise a final stress of 20 (Figure 11). Forty-two random sites concentrated around native grasses, such as sideoats grama (*Bouteloua curtipendula* (Michx.) Torr.), little bluestem (*Schizachyrium scoparium* (Michx.) Nash), inland saltgrass

(*Distichlis spicata* (L.) Greene), and blue grama as well as the majority of native forb species (Figure 11).

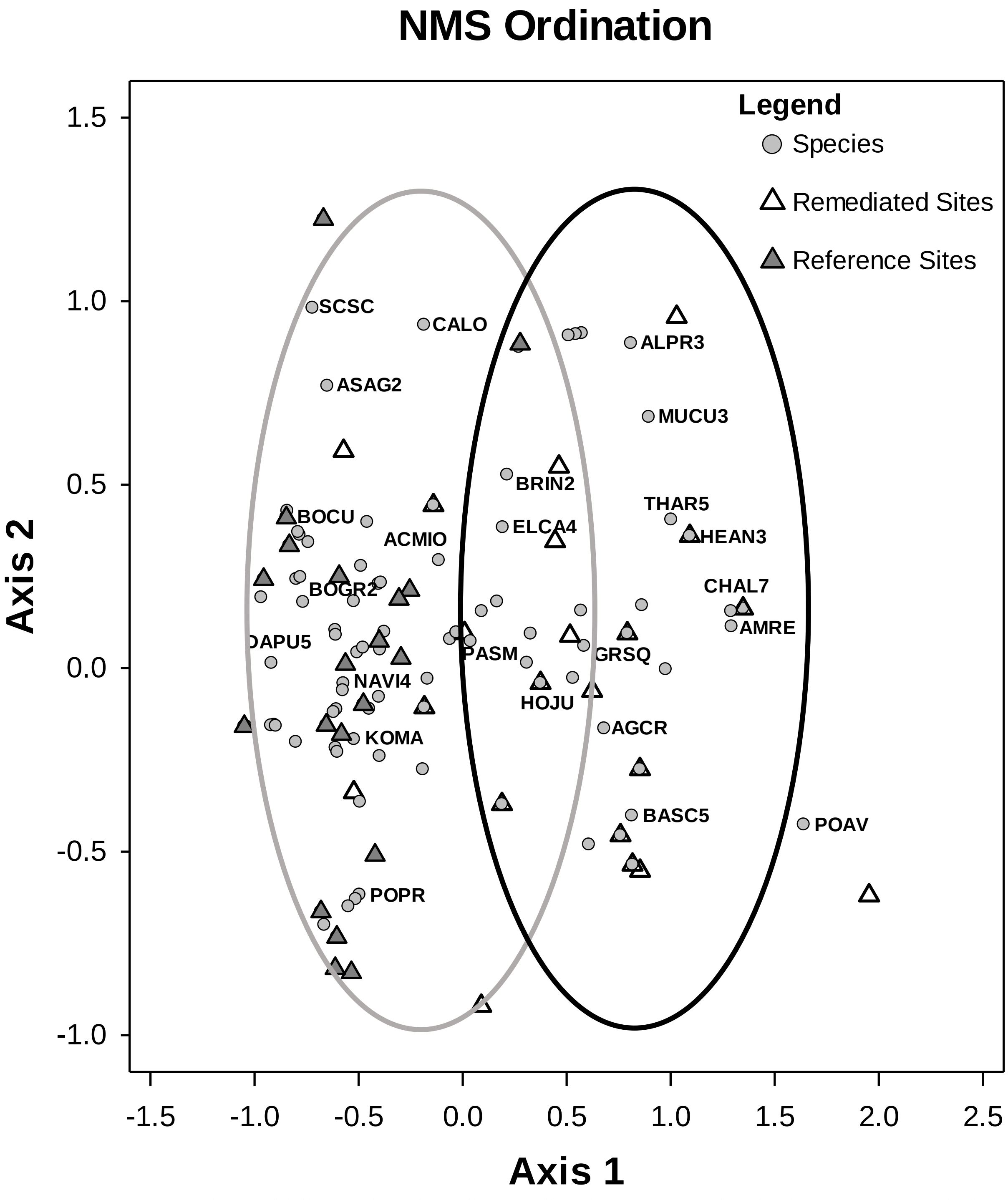

Figure 9: Non-metric multidimensional scaling ordination (NMS) displaying species and site scores on axis 1 and axis 2 across seven ecological sites on the Little Missouri National Grasslands in western North Dakota. Ovals circle reference (grey) and remediated (black) sites on the NMS graph. The area where the two ovals overlap include several halophytic species (e.g., PASMI, HOJU, and AGCR).

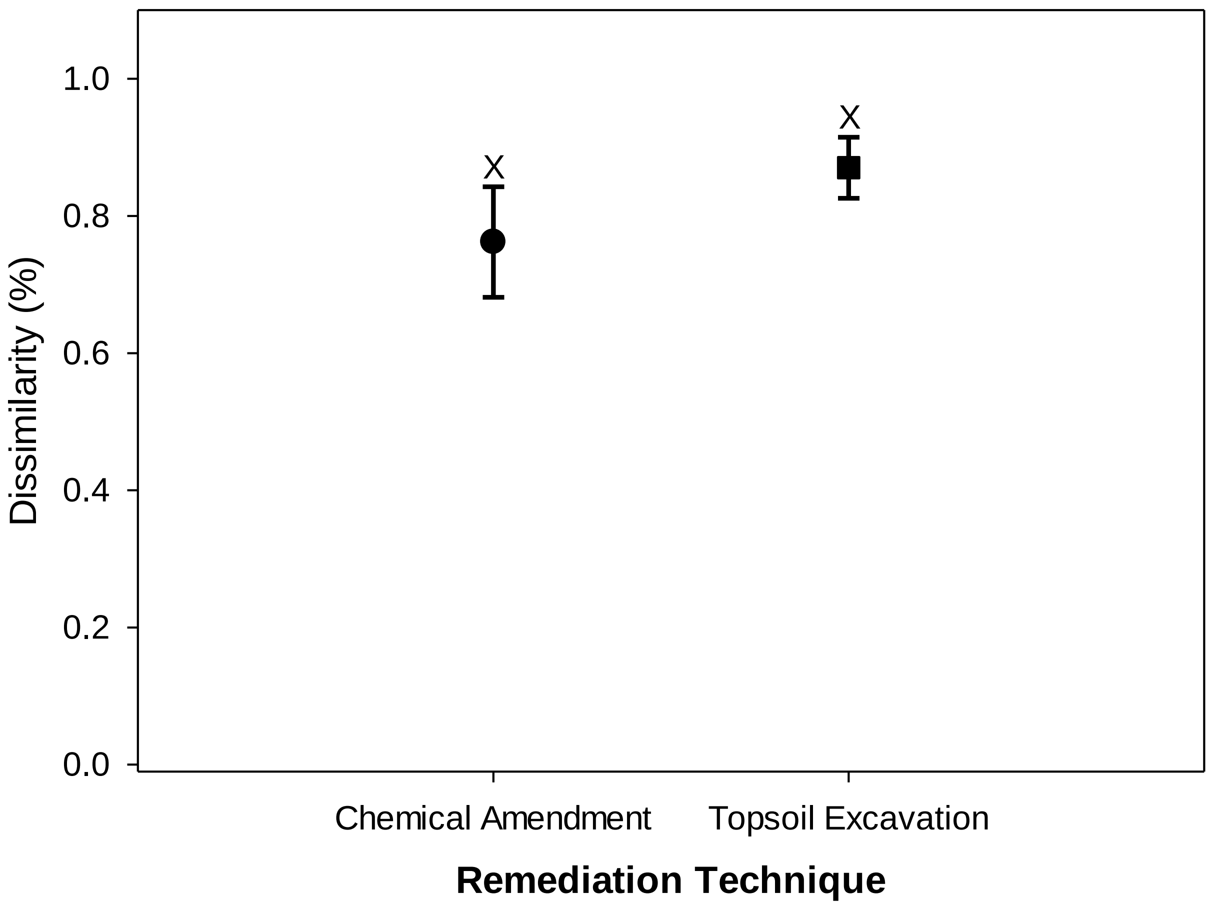

Figure 10: Sørensen dissimilarity index showing plant cover between chemical amendment and topsoil excavation techniques across seven ecological sites on the Little Missouri National Grasslands in western North Dakota.

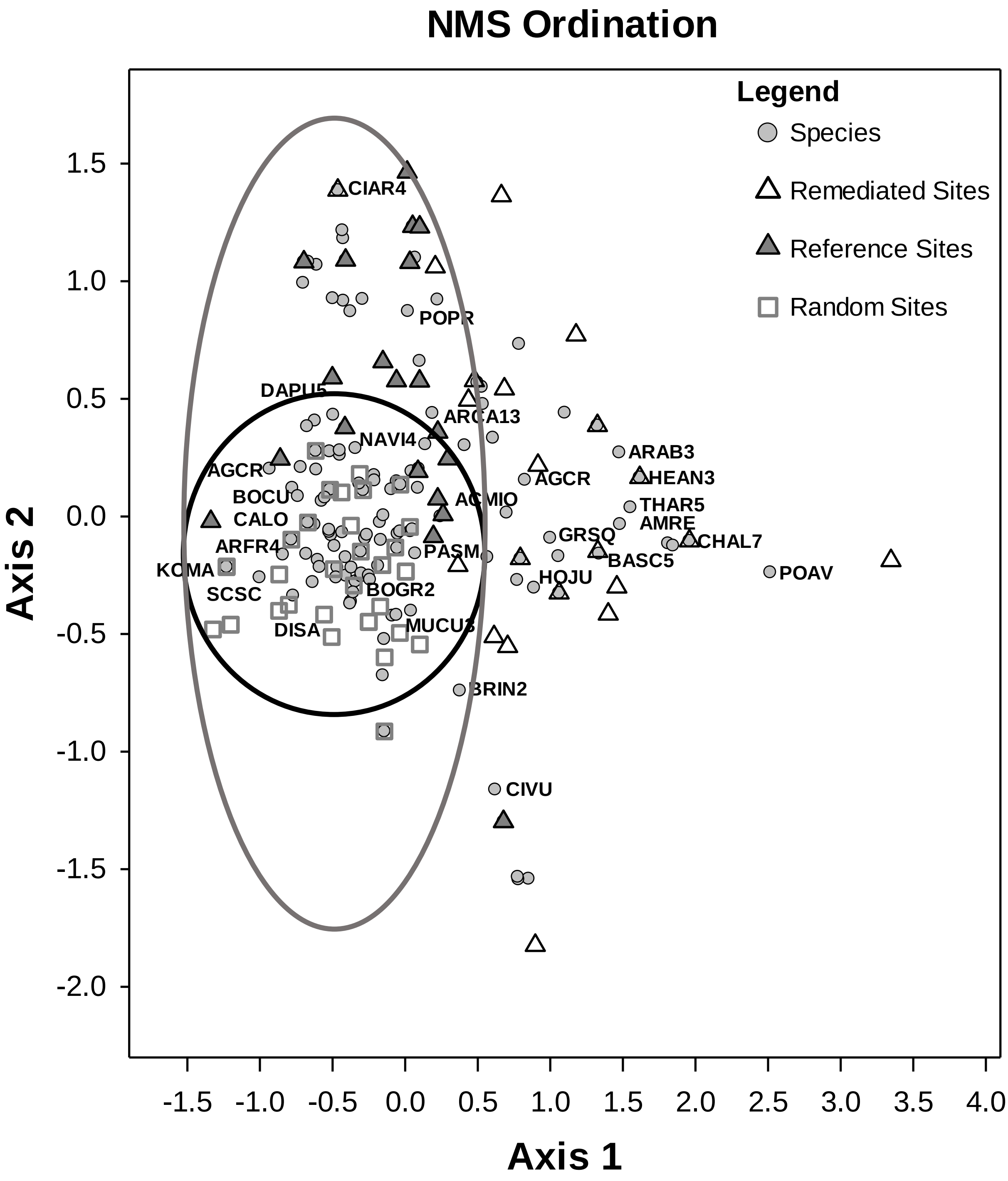

Figure 11: Non-metric multidimensional scaling ordination (NMS) displaying species and sites scores on axis 1 and axis 2 across seven ecological sites on the Little Missouri National Grasslands in western North Dakota. Ovals circle random (left -side) and majority of reference (left-side) sites on the NMS graph.

Discussion

Discharges of brine onto the soil surface can create novel ecosystems in the absence of remediation techniques. Chemical amendment and topsoil excavation techniques aim to lower the abiotic gradient to levels suitable for plant growth. Therefore, we evaluated residual brine salts, and plant composition and productivity to determine the preferred remediation technique for semi-arid rangelands. The US Forest Service expects that after four years post-remediation of brine-impacted sites, the soil EC_e levels should be comparable to reference sites and plant community is comprised of 70% native species. Our study confirmed that both remediation techniques were successful at lowering soil EC_e to facilitate natural and assisted vegetation recovery, however, vegetation on the remediated sites were not similar to reference plant communities.

Since our sampled sites were small ($\leq 45 \times 45$ m^2), the bordering edge of remediated and native prairie played an important role in species recruitment and migration. We would expect secondary succession to occur at a faster rate on smaller sites because they are in closer proximity to seed sources of intact plant communities as compared to larger sites that are further away from prairie edges (Prach and Pyšek 2001; Limb et al. 2010).

Vegetation composition and productivity mirrored EC_e data, with vegetation being similar between remediation techniques, however, vegetation was different between remediated and reference sites. A study examining soil and vegetation on a chemically remediated ($CaCl_2$) brine spill site in western North Dakota found that native plant establishment was higher on the remediated brine spill portion than on the non-remediated brine spill portion, but was not as diverse as the nearby reference site (Halvorson and Lang 1989). Residual brine salts attributed to differences in vegetation with the lowest EC_e being on the reference site and highest EC_e on the non-remediation portion (Halvorson and Lang 1989). Our results were consistent with other findings that showed chemical amendments coupled with water effectively remediated brine-affected sites (Jong 1982; Halvorson and Lang 1989; Merrill et al.1990). Though chemical amendments were effective in these studies (Jong 1982; Halvorson and Lang 1989; Merrill et al.1990), topsoil excavation is the fastest method for reducing soil contaminants (Steele and Pichtel 1998). However, there is limited research examining soil and plant recovery on *ex situ* remediated brine spill sites. Soil removal and introduction of replacement soil rapidly transforms surface soils from once vegetated areas into bare ground areas (Um and Wright 1999). Our topsoil excavation sites had three times more bare ground than chemical amendment sites because they started with bare substrate.

Life history characteristics of grassland species play an important role in species migration and propagation of disturbed grassland sites (Mcintyre et al. 1995). Succession on bare substrate is likely to start with early successional species, such as ruderals and exotics, because the environmental conditions favor their establishment (Prach and Hobbs 2008). These species usually reproduce by seed and have high dispersal capabilities, which enable them to establish on disturbed soil and take advantage of available resources first (e.g., water, light, nutrients, and space resources), outperforming later successional species (Grime 1977; Prach and Pyšek 2001). Later LMNG successional species (e.g. blue grama, sideoats grama, western wheatgrass, little bluestem, and threadleaf sedge) primarily reproduce by vegetative means (Eriksson and Jakobsson 1998), which allow grass species to fill both above and belowground gaps in grassland communities given sufficient time (Karl et al. 1999). Soil quality tends to drive early succession, whereas nutrient dynamics and life histories drive later succession stages (Gleeson and Tilman 1990). The distinction between these succession phases may explain why native grasses establishment was six times higher on chemical amendments than on topsoil excavation sites when compared to reference sites.

Natural and/or assisted perennial grass establishment is the first step in revegetating disturbed grassland communities followed by the expected natural migration of native forb species (Romo and Grilz 2002). Interestingly, native forb biomass was six times higher on topsoil excavation sites than on chemical amendment sites when compared to reference sites due to the presence of annual sunflower (*Helianthus annuus L.*) and curlycup gumweed (*Grindelia squarrosa* (Pursh) Dunal) (Limb et al. 2010). These two native annual forb species were not present on chemical amendment sites. Annual sunflower and curlycup gumweed produce greater aboveground biomass than the native forb species found primarily on the chemical amendment sites, which included wooly plantain (*Plantago patagonica* Jacq.), upright prairie coneflower (*Ratibida columnifera* (Nutt.) Wooton & Standl.), purple coneflower (*Dalea purpurea* Vent.), groundplum milkvetch (*Astragalus crassicarpus* Nutt.), white heath aster (*Sympyotrichum ericoides* (L.) G.L. Nesom), and prairie sagewort (*Artemisia frigida* Willd.). Annual sunflower and curlycup gumweed are better at colonizing contaminated soils as opposed to characteristic LMNG forb species (Olson and Fletcher 2000; Alexander and Schrag 2003).

Native shrub patches, similar to the reproductive strategies of perennial graminoid species, can migrate laterally from prairie edges to colonize disturbed sites (Romo and Grilz 2002). Silver sagebrush (*Artemisia cana* Pursh) and western snowberry (*Symphoricarpos occidentalis* Hook.) comprised 87% of native shrub biomass across all sites. Chemical amendment sites had approximately nine times higher native shrub biomass than topsoil excavation sites when compared to reference sites. Silver sagebrush and western snowberry resprout by vegetative means, enabling these shrubs to occupy both undisturbed and disturbed sites (Pelton, 1953; Wambolt et al., 1990). Similarly, native shrubs can suppress perennial grass establishment and vice versa through competition of plant resources (Kochy and Wilson 2000; Peltzer and Kochy 2001).

Exotic species are highly resilient to human-disturbances and can readily invade sites, leading to potential permanent conversions of plant communities (Stylinski and Allen 1996; DeKeyser et al. 2015). Invasive species, such as crested wheatgrass and Kentucky bluegrass, are notorious invaders of North America grasslands, creating monotypic stands and displacing native prairie species (Henderson and Naeth 2005; DeKeyser et al. 2015). Kentucky bluegrass was present on 17 of the 21 study sites, and comprised 58% of our exotic grass biomass. The presence of Kentucky bluegrass is the reason why there was no difference in exotic grass biomass between remediated and reference sites. Exotic forb biomass on both chemical amendment and topsoil excavation sites were similar due to the presence of kochia (*Bassia scoparia* (L.) A.J. Scott) and Canada thistle (*Cirsium arvense* (L.) Scop.). Kochia and Canada thistle are both considered halophytic species and can germinate and establish under high saline (NaCl) conditions (Evetts and Burnside 1972; Wilson 1979), which enable these species to invade areas where recalcitrant brine salts are present. The presence of exotic species can stymie the reclamation project and make it difficult to reach management objectives. Stylinski and Allen (1996) found that exotic species on excavated and filled disturbed sites in California shrublands prevented plant communities from recovering to their pre-disturbed states (25 years; Stylinski and Allen 1996).

Plant establishment on remediated brine spill sites is a combination of both natural and assisted vegetation. The United States Forest Service (USFS) seed mix used for oil and gas reclamation includes four LMNG species (e.g., western wheatgrass, green needlegrass, prairie sandreed (*Calamovilfa longifolia* (Hook.) Scribn.), and Canada wildrye). Green needlegrass and prairie sandreed were located on the left side of Axis 1 in closer proximity to reference sites (Figure 9). Western wheatgrass and Canada wildrye were located directly in the middle of Axis 1 and Axis 2 (Figure 9). Ideally, we would expect all four native species from the USFS seed mix to reside in the middle of the ordination. However, a variety of other species propagated our remediated sites indicating that natural revegetation exerted a stronger influence than assisted vegetation on remediated brine spill sites. The results of this study were similar to Robson et al. (2004) observations of natural migration and propagation of plant species such as, foxtail barley, western wheatgrass, kochia, annual sunflower, and curly cup gumweed, on hydrocarbon and brine contaminated sites in a semi-arid grassland.

Remediation helped to restore both the abiotic and biotic component of brine-affected sites in our study, but there are some pitfalls associated with each technique to consider before selecting a final remediation technique. Even though topsoil excavation and introduction of replacement soil does not fix the root of the problem but simply transfers it to a new location. Soil removal is an invasive method that destroys thousands of years of soil development (Bradshaw 1997), which is why *in situ* remediation has a general higher public acceptance among soil and plant ecologists than *ex situ* remediation (Khan et al. 2000). Heavy machinery associated with topsoil excavation can lead to soil compaction (Stylinski and Allen 2000), especially on soil that lacks adequate stability to resist change during mechanical compression (Angers and Caron 1998). Soil compaction further reduces soil porosity for water, gas, and nutrient fluxes to occur (Angers and Caron 1998; Bronick and Lal 2005), and prevent plant roots from penetrating through soil layers (Milchunas et al. 1999; Stylinski and Allen 2000). Replacement soil may also differ in soil properties (e.g., soil texture, organic matter, and nutrient status) from the surrounding area and yield a different plant community than what previously existed. Soil texture influences plant and soil water relationships and is the primary factor in defining rangeland plant communities (Barnes et al. 1983; Milchunas et al. 1999). Soils dominated with coarser particles (i.e. sand) have larger soil pores and lower water holding capacity to support deep-rooted C_4 species (Barnes and Harrison 1982). Whereas, soils dominated by finer, textured particles, such as silt and clay, have smaller soil pores and display higher water holding capabilities that benefit shallow-rooted C_3 species (Barnes and Harrison 1982).

Soil replacement may also unintentionally contain an exotic seed bank, introducing new species that can germinate and migrate into the surrounding area. Replacement soil from a local or nearby source is desirable because it reduces the likelihood of introducing new species. However, excavation for replacement soil on public land is illegal, requiring replacement soil to come from private sources. Transportation and disposal of brine-contaminated soil can lead to social and ecological challenges, by requiring designated hazardous waste landfills to be within close proximity to excavated sites. The two designated hazardous waste landfills in North Dakota are not equipped to handle the high influx of soil contaminated by oil and gas activities, which has led to the illegal dumping of contaminated soil in municipal landfills. These illegal dumpings could lead to the migration of brine-contaminants from these landfills into adjacent areas. Despite its ecological implications, topsoil excavation is a common remediation technique even though it is an unsustainable method.

Alternatively, chemical amendments rely on intact soil structure to displace Na^+ ions on soil cation exchange sites and replace it with Ca^{2+}ions. The main pitfalls to chemical amendments is that they are often intensive and ineffective without a supplemental water source in semi-arid to arid climates (Jury and Weeks 1978). Leached brine salts can also travel upward during periods of dryness, leading to resalinization of surface soil (Thimm 1990; Harris et al. 2005), or perched salt-laden water may travel laterally with the curvature of the landscape and resurface in a new location (Murphy et al. 1988; Harris et al. 2005). However, these pitfalls are less cumbersome than trying to overcome the loss of original soil and/or mixing of soil horizons that occurred during topsoil excavation. Soil structure is important for plant productivity because it influences root distribution (Pardo et al. 2005). Plant roots that are able to penetrate through soil layers to extract water and nutrients from the soil matrix will continue to grow and develop, whereas compacted soil layers restrict plant roots from accessing water and nutrients (Bronick and Lal 2005). Most importantly, both above and belowground plant parts protect soil from erosional hazards, while contributing organic materials via species turnover to improve site conditions and increase soil fertility. We would expect plant succession to occur at a slower rate on soil that lacks adequate soil structure and presents an additional barrier for plants to overcome. Soils that start with bare substrate also tend to be nutrient poor due to lack of nitrogen, which limits plant productivity and is more in line with early succession processes (Gleeson and Tilman 1990). Additionally, external calcium (Ca^{2+}) may facilitate higher potassium (K^{+}) selectivity over sodium (Na^{+}) ion uptake in the soil matrix, which can help plants gradually adapt to salt stress (NaCl) (Liu and Zhu 1997).

Conclusions

Successful brine spill remediation removes the majority of brine salts from the plant root zone to facilitate plant establishment. Since natural attenuation in semi-arid to arid areas is not effective, remediation via chemical amendments and topsoil excavation can ameliorate site conditions. Both remediation techniques were successful at lowering EC_e levels to allow vegetation establishment to occur in semi-arid rangelands. Since soil EC_e was not a delimiting factor between remediation techniques in this study, we believe the use of chemical amendments are the preferable remediation option on small spill sites because it maintains soil integrity and does not generate soil waste. Although there are some pitfalls to this technique, chemical amendments isolate the problem on sites as opposed to topsoil excavation that translocate contaminated soil to a disposal location, where it can potentially have negative effects on the surrounding ecosystems. Efficiency and sustainability are two factors to consider before selecting a remediation technique.

Succession on oil and gas contaminated sites is slow in semi-arid to arid climates, where limited precipitation and hot temperatures can delay plant recovery on remediated brine spill sites. Ruderal and exotic species are likely to dominate remediated brine spill sites during early successional stages, especially on topsoil excavation sites that start with bare substrate. Some of these early successional species help stabilize soil and improve site conditions via species turnover to facilitate the establishment of later successional species. However, the presence of exotic species such as, Kentucky bluegrass, crested wheatgrass, and Canada thistle, can lead to permanent changes in plant cover and prevent the site from returning to pre-spill conditions. Although the act of brine discharged onto the soil surface is usually one discrete event, returning native plant productivity to these remediated brine spill sites is slow and in some cases highly unlikely. Future work should focus on preventing brine spills as opposed to reacting to them.

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GENERAL CONCLUSIONS

Brine spills can create novel ecosystems in the absence of remediation techniques. Natural attenuation does not lessen the negative impacts of brine overtime in semi-arid to arid regions, at least not on a practical timescale. Limited precipitation in these regions prevents the downward leaching of salt ions below the plant root zone. Human intervention through topsoil excavation and chemical amendments is necessary to remove/lower the amount of brine salts to levels suitable for plant growth. Salt tolerant species (i.e. halophytes) are desirable for revegetating remediated brine spill sites because they are naturally present in the environment and can uptake residual brine salts through plant roots during dry periods when salt-laden water moves from upper to lower soil depths via capillary action to meet atmospheric demand.

Halophytes are adapted to completing their lifecycle in the presence of salt stress, and can desalinate and stabilize soil to restore the biotic component of salt-degraded sites. The results of the greenhouse experiment display the potential of salt sensitive species (i.e. glycophytes) and salt tolerant species (i.e. halophytes) for revegetating remediated sites. Glycophytes (e.g., *Poa pratensis*, *Nassella viridula*, *Bouteloua gracilis*, and *Schizachyrium scoparium*) exhibited lower brine thresholds 9.70 and 18.6 dS m^{-1}) than known halophytic species (18.6 and 34.6 dS m^{-1}; e.g., *Pascopyrum smithii*, *Hordeum jubatum*, *Puccinellia nuttalliana*, *Distichilis spicata*, and *Sporobolus airoides*). We detected no brine threshold for two halophytes (*Hordeum jubatum* L. and *Puccinellia nuttalliana* (Schult.) Hitchc.) at both growth stages in this greenhouse experiment. Declines in above-and-belowground weights mirrored increases in soil EC_e concentrations, with lower biomass weights observed at the seedling stage for both halophytes and glycophytes. The results of the greenhouse study aid oil and gas personnel and environmental consultants in identifying EC_e benchmarks for plant growth. Additionally, the native halophytes examined in this study are suitable species for revegetating remediated brine spill sites and diversifying oil and gas reclamation seed mixes.

Brine spill remediation techniques may attribute to differences in plant community assembly and affect how sites undergo secondary succession. Our study concluded there was no difference ($p > 0.05$) in soil EC_e between chemical amendments and topsoil excavation techniques to the 60 cm depth. Bare ground cover was different ($p < 0.05$) between remediation techniques, but litter cover was not different between ($p \geq 0.05$) remediation techniques. Biomass for all functional plant groups with the exception of native forbs was not different ($p \geq 0.05$) between remediation techniques. Species richness and evenness, and Simpson's diversity was not different ($p \geq 0.05$) between remediation techniques. Additionally, the Sørensen Dissimilarity Index was not different ($p \geq 0.05$) between remediation techniques. Exotic species establishment was more prevalent on remediated brine spill sites as indicated by the NMS ordination and PerMANOVA. Native species comprised higher proportions of reference and random sites, random sites were more diverse than references sites likely because they were further away from oil and gas related disturbances.

Our field study determined that chemical amendments and topsoil excavation are both effective techniques to remove/minimize brine salts across seven ecological sites with different soil properties (e.g., texture, nutrient status, and organic matter). Additionally, our research identifies ruderal and exotic species that are likely to establish on remediated brine spill sites and several invasives species (e.g., *Poa pratensis*, *Agropyron cristatum*, and *Cirsium arvense*) that may stymie the reclamation process. We also discuss some of the pitfalls associated with each remediation techniques so that oil and gas personnel and environmental consultants can effectively evaluate each remediation technique and choose a remediation technique based on efficacy and sustainability.

APPENDIX A. CHAPTER 2 TABLES

Table A1: List of sampled remediated brine spill sites on the Little Missouri National Grasslands in western North Dakota in the summer of 2015; list includes spill date, cause of spill, quantity of brine spilt (bbls), respective remediation techniques, data of remediation, and if reseeding occurred.

Remediated Site	Spill Date	Cause of Spill	Quantity (bbls)	Remediation Technique	Remediation Date	Reseeding Yes or No
1	11/4/2007	Tank Battery Overflow	60	Chemical Amendment	11/5/2007	No
2	Unk.[†]	Pipeline leak	Unk.	Chemical Amendment	6/14/2012	Yes
3	3/21/2008	Tank Battery Overflow	100	Chemical Amendment	7/22/2008	Yes
4	9/22/2008	Pipeline leak	690	Chemical Amendment	9/22/2008	Yes
5	4/14/2010	Pipeline leak	Unk.	Chemical Amendment	4/16/2010	Yes
6	9/1/2011	Pipeline leak	40	Chemical Amendment	9/2/2011	Yes
7	3/21/2011	Tank Battery Overflow	70	Chemical Amendment	3/28/2011	Yes
8	Unk.	Tank Battery Overflow	Unk.	Chemical Amendment	9/22/2014	No
9	10/23/2013	Pipeline Leak	150	Chemical Amendment	10/26/2013	Yes
10	12/14/2011	Tank Battery Overflow	220	Chemical Amendment	07/21/2011	No
11	12/14/2011	Tank Battery Overflow	Unk.	Topsoil Excavation	07/21/2011	No
12	06/22/2014	Tank Battery Overflow	10	Topsoil Excavation	6/30/2014	Yes
13	10/6/2011	Pipeline leak	3	Topsoil Excavation	10/08/2011	Yes
14	12/17/2011	Pipeline Leak	60	Topsoil Excavation	4/28/2012	Yes
15	8/24/2009 11/26/2008 11/26/2008	Pipeline Leak	22 11 5	Topsoil Excavation	8/27/2009 6/02/2009 6/02/2009	Yes
16	6/2/2013	Tank Battery Overflow	15	Topsoil Excavation	7/31/2013	Yes
17	4/22/2007 10/7/2009 10/31/2013 8/18/2014	Pipeline Leak	40 100 70 65	Topsoil Excavation	5/01/2007 10/09/2009 11/05/2013 8/19/2014	Yes
18	1/28/2013	Tank Battery Overflow	13	Topsoil Excavation	1/28/2013	Yes
19	11/25/2013	Pipeline Leak	16	Topsoil Excavation	11/27/2013	Yes
20	11/5/2012	Tank Battery Overflow	299	Topsoil Excavation	7/19/2013	Yes
21	10/23/2013	Pipeline Leak	150	Topsoil Excavation	12/01/2015	No

[†]=Unk. =Unknown information

Table A2: USDA soil texture classifications for topsoil excavation sites (REM) and the paired reference sites (REF) across seven ecological sites on the Little Missouri National Grasslands in western North Dakota

	Percent Sand		Percent Silt		Percent Clay		USDA Textural Class[†]	
Site	REF[‡]	REM	REF	REM	REF	REM	REF	REM
11	48.0	30.3	32.4	38.7	19.6	31.0	Loam	Clay Loam
12	22.3	20.3	51.3	73.3	26.4	6.4	Silt Loam	Silt Loam
13	5.9	34.1	64.1	32.9	30.0	33.0	Silty Clay Loam	Clay Loam
14	25.4	58.6	52.8	25.2	21.8	16.2	Silt Loam	Sandy Loam
15	13.3	23.6	60.9	50.6	25.8	25.8	Silt Loam	Silt Loam
16	55.1	35.0	32.5	33.0	12.4	32.0	Sandy Loam	Clay Loam
17	5.8	52.5	56.0	28.3	38.2	19.2	Silty Clay Loam	Sandy Loam
18	38.5	13.1	43.9	49.9	17.6	37.0	Loam	Silty Clay Loam
19	10.8	22.5	57.6	53.9	31.6	23.6	Silty Clay Loam	Silt Loam
20	68.2	20.2	24.8	53.6	7.0	26.2	Sandy Loam	Silt Loam
21	40.7	30.5	39.5	47.9	19.8	21.6	Loam	Loam

[†]= Black, 1965

[‡]= REF= Reference site, REM= Remediation site

Table A3: Saturated Paste extract (EC_e) electrical conductivity for topsoil excavation sites (REM) and the paired reference sites (REF) across seven ecological sites on the Little Missouri National Grasslands in western North Dakota.

		EC_e[§] (dS m^{-1})		
Treatment	Site ID	0-15cm	15-30cm	30-60cm
Chemical	REF 1[‡]	0.69[†]	2.12	2.73
Amendment	REM 1[‡]	0.68	0.97	3.19
Chemical	REF 2	1.30	1.15	2.94
Amendment	REM 2	1.58	1.43	1.71
Chemical	REF 3	0.87	0.75	6.21
Amendment	REM 3	1.68	3.68	6.33
Chemical	REF 4	0.94	0.97	3.88
Amendment	REM 4	1.78	2.49	8.39
Chemical	REF 5	0.65	0.54	0.97
Amendment	REM 5	3.91	6.48	8.95
Chemical	REF 6	0.78	0.78	3.54
Amendment	REM 6	8.89	15.2	12.8
Chemical	REF 7	0.88	0.68	0.65
Amendment	REM 7	1.69	1.48	1.83
Chemical	REF 8	0.97	2.43	6.93
Amendment	REM 8	4.93	6.76	8.85
Chemical	REF 9	0.30	0.24	0.21
Amendment	REM 9	2.14	5.31	13.7
Chemical	REF 10	0.90	1.18	2.51
Amendment	REM 10	10.6	8.40	9.40
Topsoil	REF 11	0.90	1.18	2.51
Excavation	REM 11	2.51	4.08	8.34
Topsoil	REF 12	1.41	9.13	18.5
Excavation	REM 12	8.00	18.1	25.6
Topsoil	REF 13	1.23	1.25	6.65
Excavation	REM 13	1.62	3.67	6.77
Topsoil	REF 14	0.46	3.79	27.1
Excavation	REM 14	3.90	5.95	14.5
Topsoil	REF 15	1.86	2.19	8.17
Excavation	REM 15	1.48	3.28	9.15
Topsoil	REF 16	0.31	0.34	0.98
Excavation	REM 16	2.32	5.58	3.14
Topsoil	REF 17	0.85	0.80	1.58
Excavation	REM 17	1.48	1.41	1.34
Topsoil	REF 18	0.85	0.84	0.85
Excavation	REM 18	3.51	6.79	7.13
Topsoil	REF 19	0.85	0.77	1.23
Excavation	REM 19	4.53	2.12	3.33
Topsoil	REF 20	0.38	0.79	3.17
Excavation	REM 20	4.19	13.1	21.6
Topsoil	REF 21	3.63	19.0	28.7
Excavation	REM 21	2.14	6.40	27.6

[§]= Electrical conductivity from a saturated paste extract

[†]= Klaustermeier et al. 2016

[‡]= REF= Reference site, REM= Remediation site

Table A4: Biomass and ground cover data for topsoil excavation sites (REM) and the paired reference sites (REF) across seven ecological sites on the Little Missouri National Grasslands in western North Dakota

Treatment	Site ID	Native Grass	Exotic Grass	Native Forb	Exotic Forb	Native Shrub	Litter[§]	Bare Ground
		----------------------kg/ha----------------------					------%------	
Chemical	REF 1[‡]	473	38.2	123	0.60	110	7.40	0.9
Amendment	REM 1	80.2	42.4	87.8	4.20	740	9.00	33.5
Chemical	REF 2	149	123	130	11	204	7.53	6.13
Amendment	REM 2	5.25	517	6.2	1040	5.65	16.0	7.28
Chemical	REF 3	965	46.9	76.3	30.4	75.1	2.13	2.13
Amendment	REM 3	112	867	38.6	130	156	16.6	3.56
Chemical	REF 4	860	297	28.1	0.00	0.00	11.7	8.97
Amendment	REM 4	833	2.33	22.13	0.00	6.20	1.2	35.7
Chemical	REF 5	326	0.00	234	0.00	1853	3.85	0.50
Amendment	REM 5	1224	212	4.70	0.80	23.6	22.0	0.50
Chemical	REF 6	967	0.00	16.2	0.00	400	10.0	4.00
Amendment	REM 6	478	0.00	2.40	492	102	8.60	51.0
Chemical	REF 7	16.3	99.4	117	129	704	30.0	0.50
Amendment	REM 7	0.00	162	46.6	205	821	3.63	9.75
Chemical	REF 8	87.1	1099	55.5	138	23.9	19.8	0.50
Amendment	REM 8	30.0	1.53	0.60	1365	0.00	0.50	40.4
Chemical	REF 9	1037	4.30	173	1.30	48.4	6.94	0.63
Amendment	REM 9	97.6	1338	20.0	4.6	0.00	28.2	0.75
Chemical	REF 10	1780	453	41.3	18.4	0.00	12.8	2.54
Amendment	REM 10	3523	62.8	0.00	2.33	0.00	24.2	0.50
Topsoil	REF 11	1780	453	41.3	18.4	0.00	12.8	2.54
Excavation	REM 11	75.1	65.8	615	414	0.00	4.50	41.7
Topsoil	REF 12	110	858	4.40	2.80	0.00	8.10	0.50
Excavation	REM 12	0.20	0.00	0.00	75.4	0.00	0.50	90.4
Topsoil	REF 13	507	10.0	54.0	0.00	259	1.70	15.2
Excavation	REM 13	1116	4950	3248	1458	0.00	0.50	37.0
Topsoil	REF 14	0	1208	58.8	0.00	42.6	24.0	0.50
Excavation	REM 14	23.0	116	0.00	258	0.00	0.50	72.7
Topsoil	REF 15	1007	53.2	69.8	0.00	174	7.70	1.70
Excavation	REM 15	49.0	647	15.4	8.20	237	5.40	12.9
Topsoil	REF 16	1154	4.30	106	0.00	18.3	1.30	4.85
Excavation	REM 16	198	30.2	204	381	0.00	1.20	54.0
Topsoil	REF 17	301	175	42.6	1.50	683	6.46	0.75
Excavation	REM 17	35.3	0.25	0.75	1215	0.00	0.50	57.3
Topsoil	REF 18	510	24.2	139	0.00	97.2	5.40	0.50
Excavation	REM 18	117	5.60	271	614	0.00	1.10	58.7
Topsoil	REF 19	848	1.10	29.0	0.00	145	6.79	2.50
Excavation	REM 19	199	41.7	0.00	155	0.00	0.50	64.6
Topsoil	REF 20	725	6.63	42.1	12.0	142	6.00	10.3
Excavation	REM 20	292	0.00	3.75	0.63	0.00	0.50	73.8
Topsoil	REF 21	157	1093	6.40	0.00	3.60	27.0	0.50
Excavation	REM 21	0.00	217	0.00	8.60	0.00	1.70	82.1