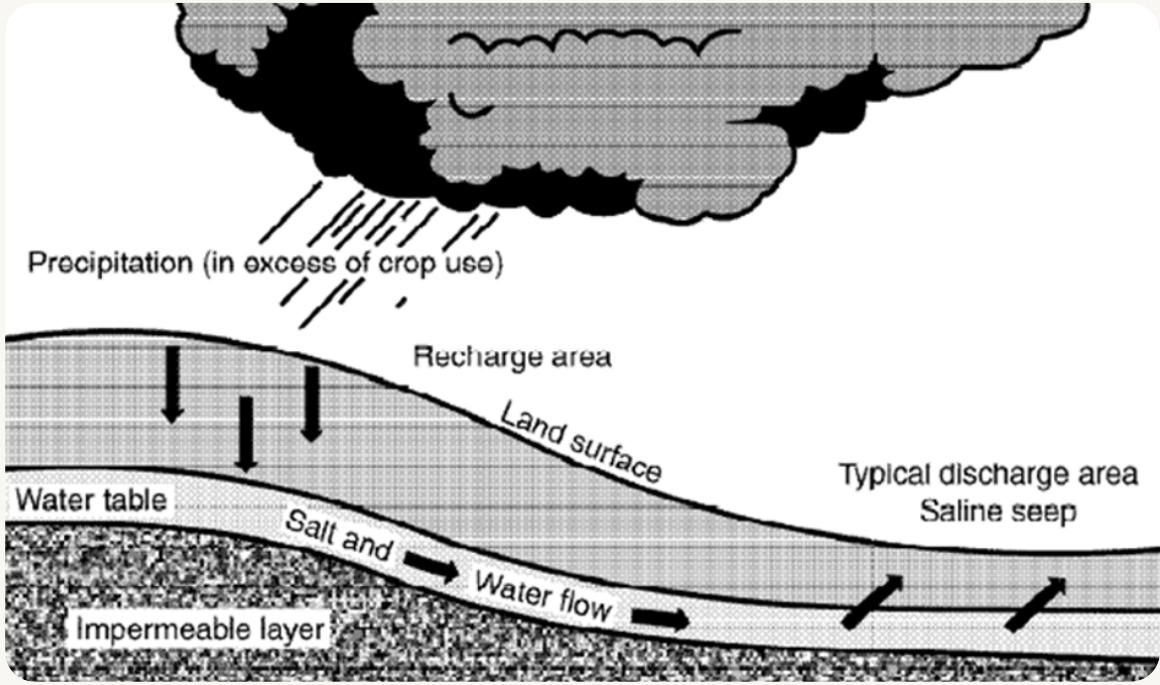
Soil Response to Produced Water Mixing: A Comparative Analysis of Saline and Non-Saline Soils in PHREEQC

By Chantel Mertz

NDSU Geochemistry
May, 2025

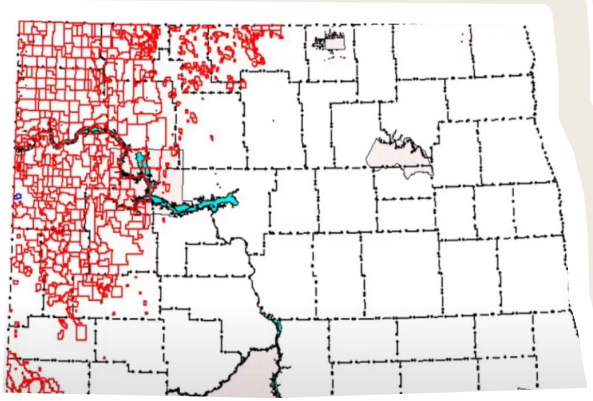
Natural salinity

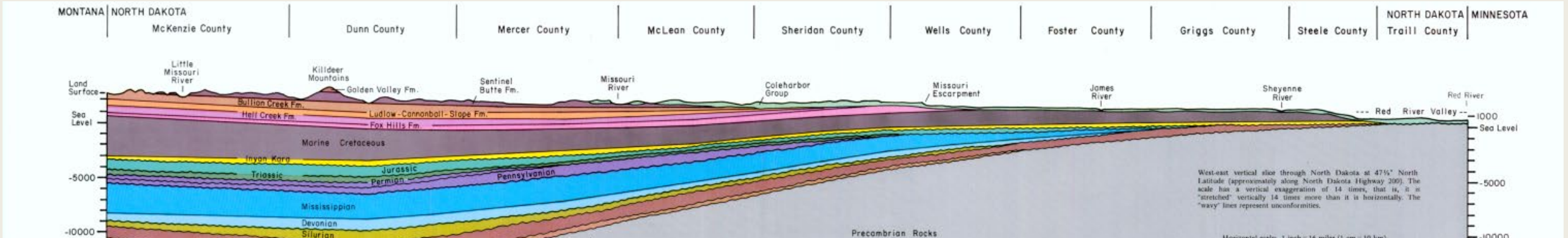
- Within the past 100,000 years we have had several glaciations
- These glaciers ground and moved limestone ($CaCO_3$) and granite from Canada into North Dakota
- As a result most of North Dakota has carbonate as well as sulfate-based salts
- Salts come up from the ground water through capillary rise salinizing the soil
- This occurs in areas with greater evaporation than precipitation



Produced Water Spills

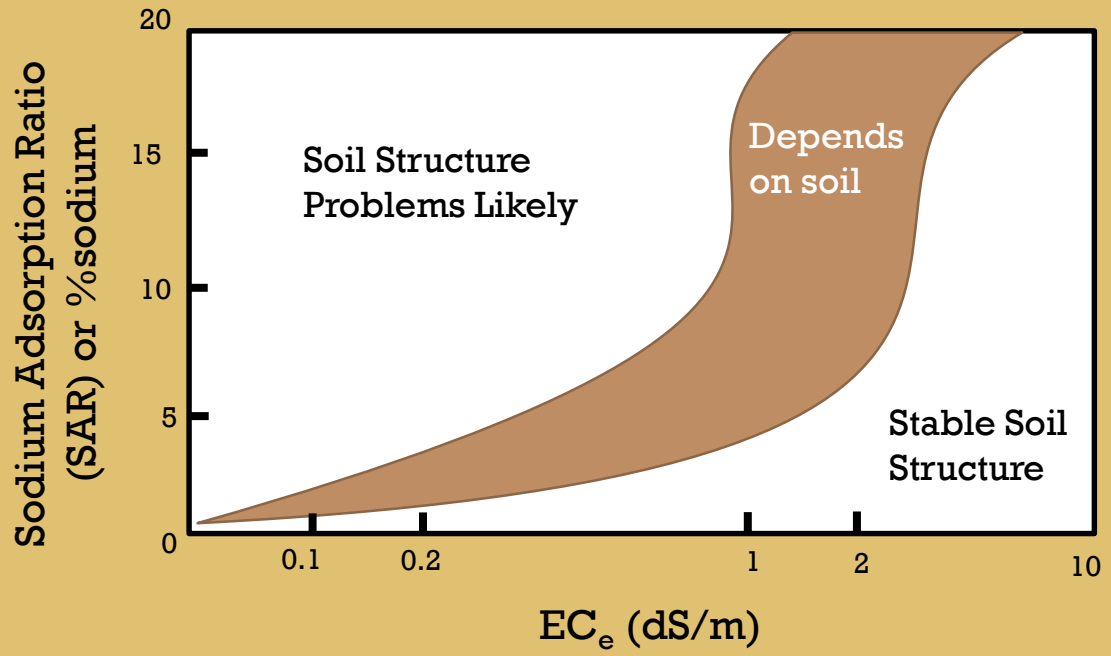
- Produced water is a byproduct of the oil and gas industry
- It is primarily composed of water, salts, sand, oil, and drilling chemicals
- Sodium chloride (NaCl) composes about 90% of these salts
- Between 2021 and 2023, over 1,026 produced water spills were reported, resulting in a total of 7,329,120 gallons of brine spilled





Effects of Salinity

- High concentrations of salts can negatively affect soil structure and plant growth
- Salinity is often measured using electrical conductivity
- Electrical conductivity (EC) refers to the ability of a substance to conduct an electrical current over a defined area
- Reported as deciSiemens per meter (dS/m)
- Pure water has no electrical conductivity



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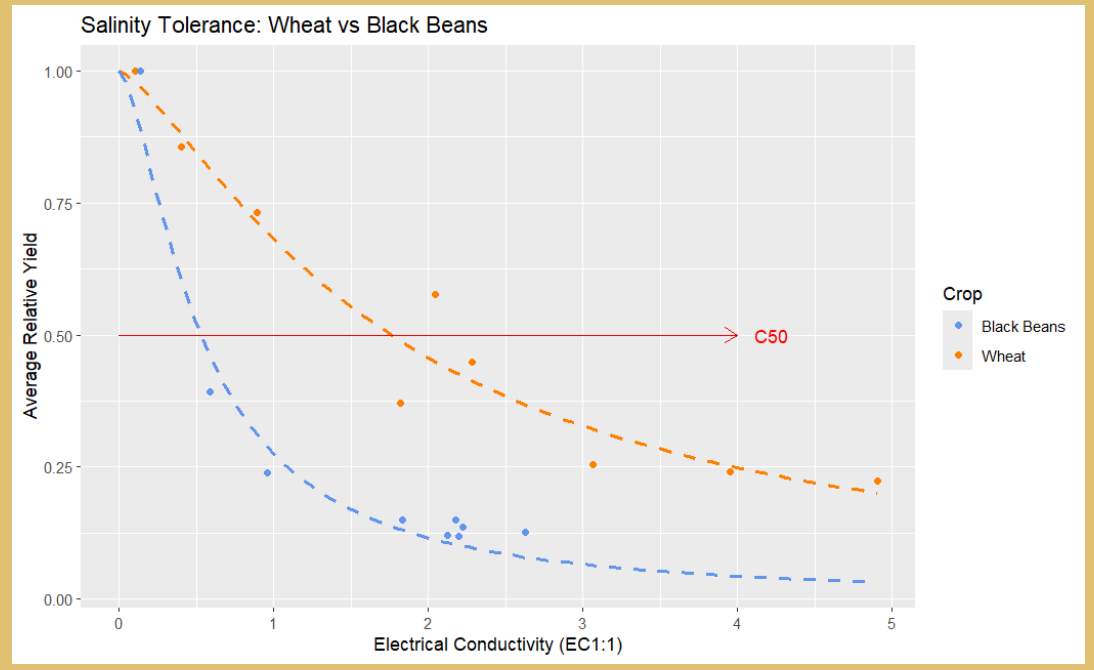
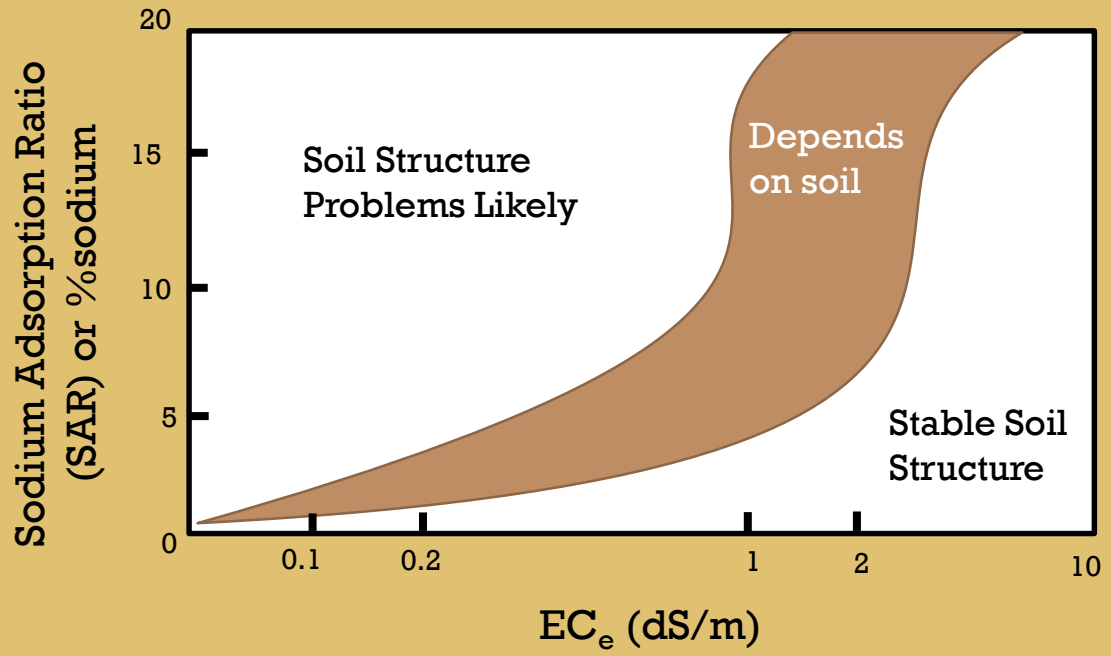
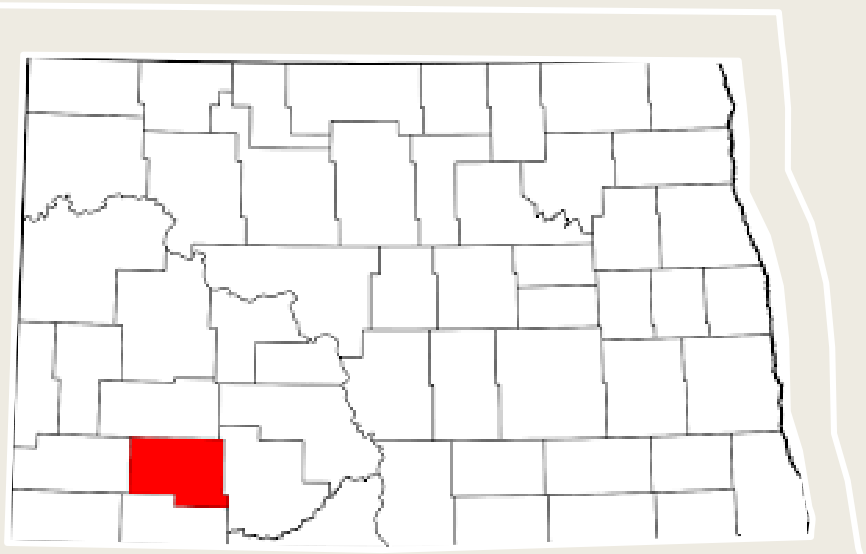




Key Reference



Geoderma, 37 (1986) 295—305
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

IONIC COMPOSITION AND DISTRIBUTION IN SALINE SEEPS OF SOUTHWESTERN NORTH DAKOTA, U.S.A.*[1]

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(Received September 6, 1985; accepted after revision March 13, 1986)

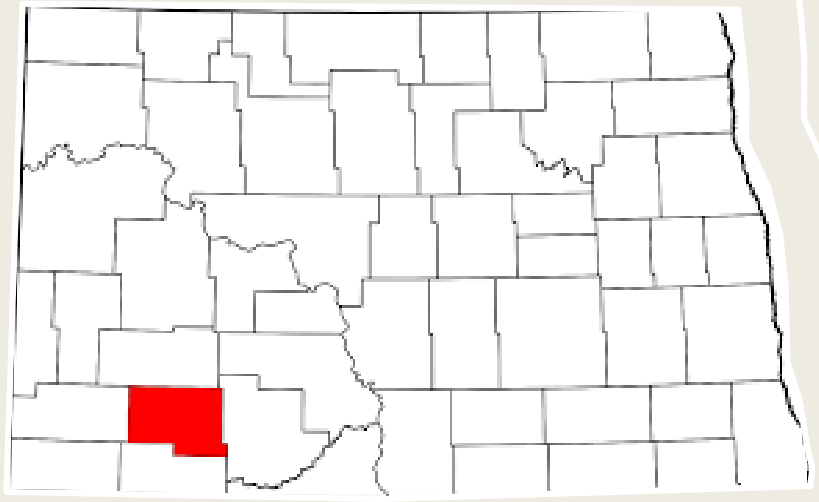
ABSTRACT

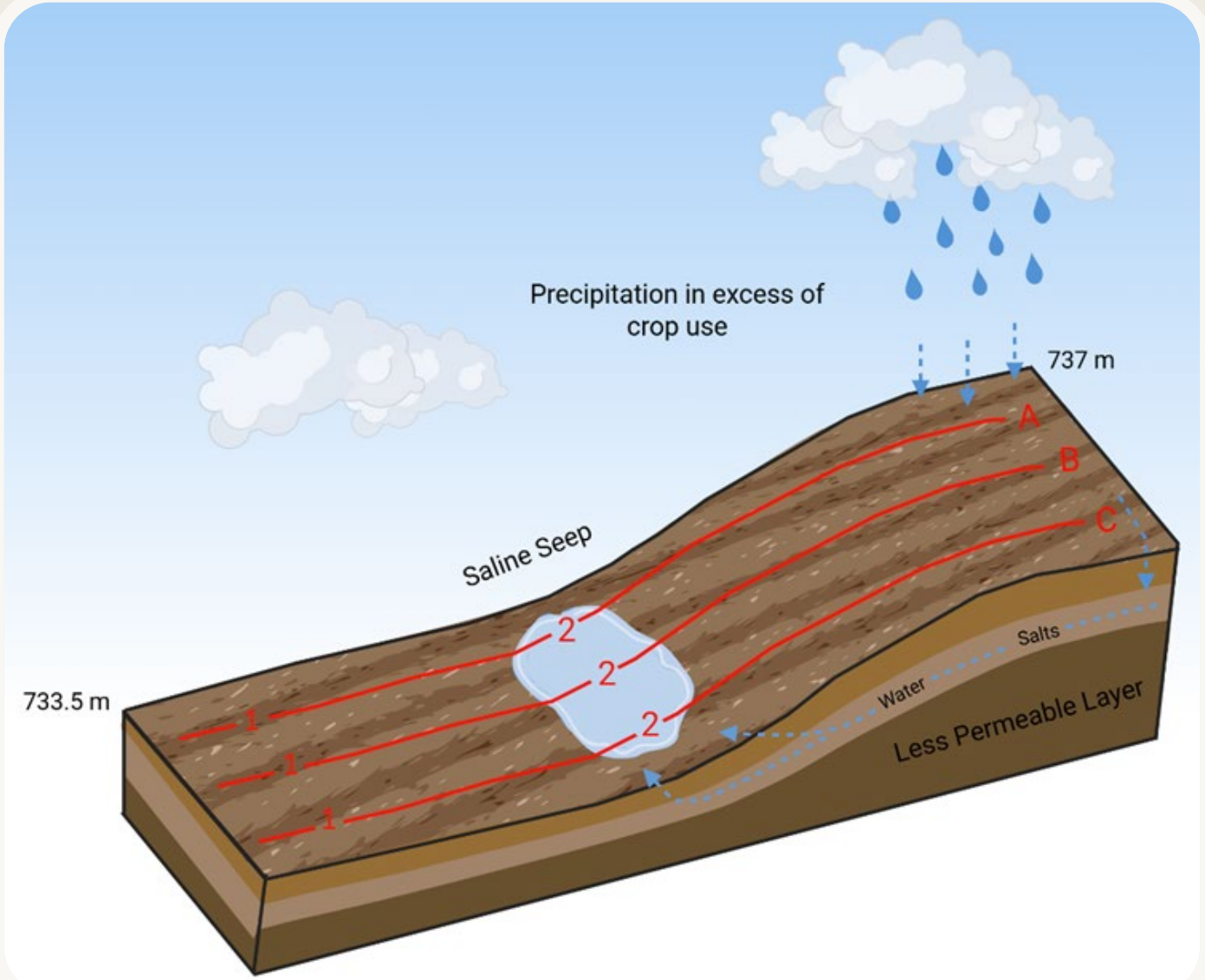
Timpson, M.E. and Richardson, J.L., 1986. Ionic composition and distribution in saline seeps of southwestern North Dakota, U.S.A. Geoderma, 37: 295—305.

Saline seeps, a common problem in the Northern Great Plains, were studied at four sites in southwestern North Dakota. Saturation extracts within seeps were dominated by sodium, magnesium, and sulfate. Where present, gypsum controlled calcium concentrations. Ionic distributions within and around seeps were influenced by precipitation and re-solution reactions, freeze—thaw phenomena, and ion pairing. Ion pairing reduced Ca^{2+} and Mg^{2+} activities to a greater extent than Na^{+}, resulting in elevated SAR levels in seeps and surrounding soils. Dryland salinity resulted in a form of desertification around seep areas.

Sample Locations

- Sample 1- Unaffected Soil
- Sample 2 - Saline Soil





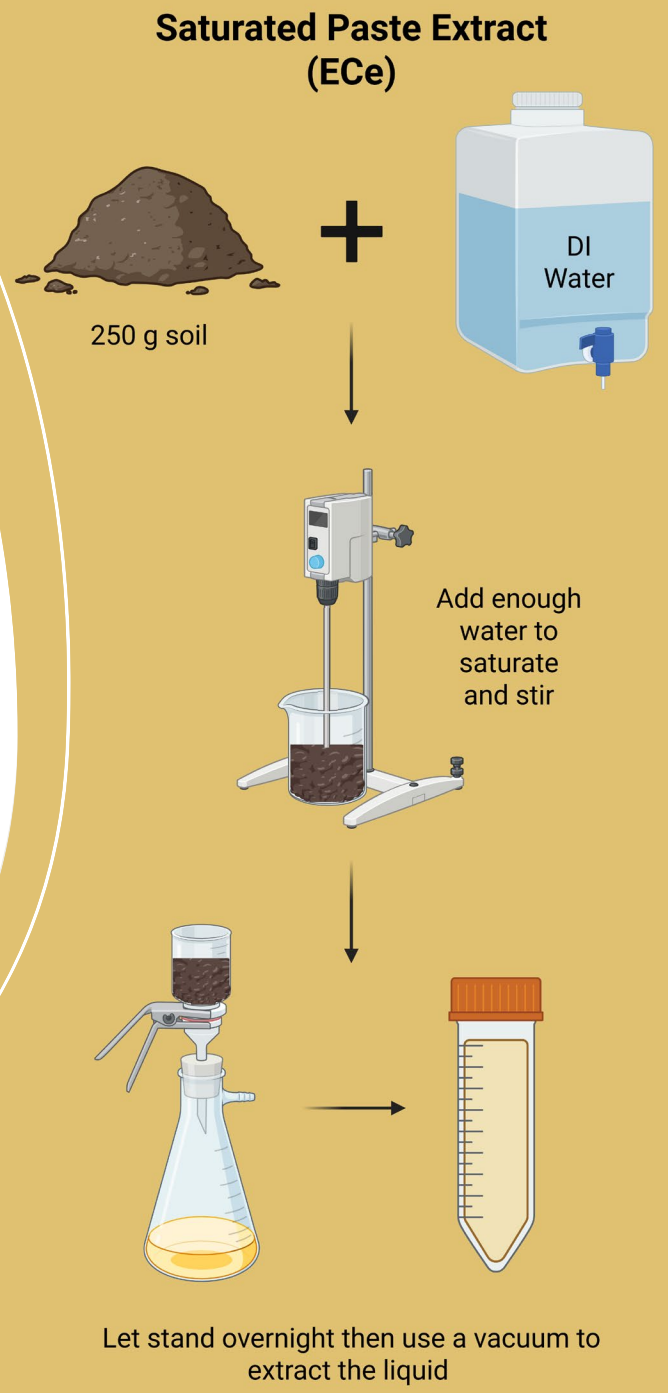
Sample Information

Produced Water Sample

- Analysis from the ND Department of Environmental Quality
- Likely from the Williston Basin

Saline & Unaffected Soils

- From Hettinger County, ND
- Formed from sandy alluvium from the Cannonball River
- Rests on the Bullion Creek Formation
- Average of three 0-6 inch soil samples

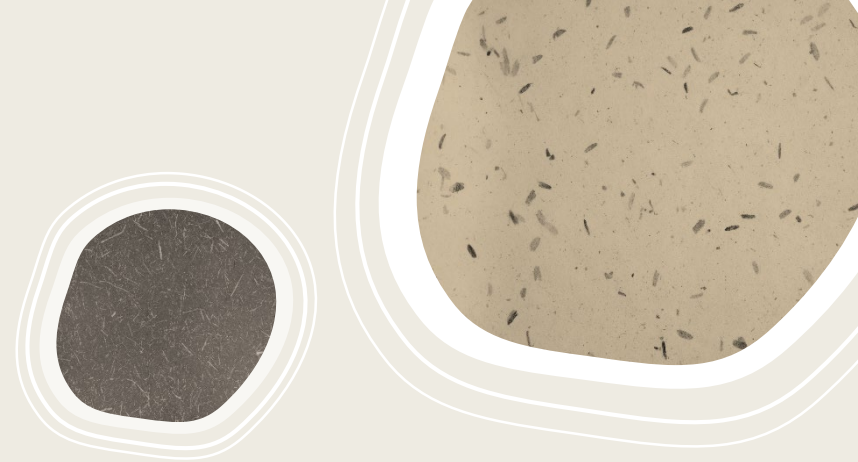


General Sample Information

Sample	Electrical Conductivity	Ca^{2+}	Na^{+}	SO_4^{2-}	Cl^{-}
	dS/m	----------mg/L----------			
Unaffected Soil	1.8	441	92	1,441	103
Saline Soil	12	882	2,276	16,137	124
Produced Water	207	8,420	83,900	0	139,000

Part 1: Unaffected Soil vs Saline Soil

PHREEQC Inputs



Unaffected Soil

```
TITLE Mertz Project, part A.--Speciation via Saturated Extract
of Unaffected Soil.
SOLUTION 1  Unaffected Soil
    temp      25
    pH        6.5
    units     mmol/kgw
    density   1
    C(4)      3.3
    Ca        11
    Cl        2.9
    K         1.4
    Mg        4.9
    Na        4
    S(6)      15
    -water    1 # kg

SAVE solution 1
END
```

Saline Soil

```
TITLE Mertz Project, part B.--Speciation via Saturated Extract
of Saline Soil.
SOLUTION 2 Saline Soil
    temp      25
    pH        7.8
    units     mmol/kgw
    density   1
    C(4)      4.4
    Ca        22
    Cl        3.5
    K         1.5
    Mg        52
    Na        99
    S(6)      168
    -water    1 # kg

SAVE solution 2
END
```

Activity Coefficients

- The Pitzer equation was used to determine the activity coefficients, as it is most accurate for solutions with high ionic strengths
- Originally, the Debeye-Huckel equation was used, it portrayed results closer to the published values
- Activity coefficients for Ca^{2+} and Mg^{2+} deviated from published values, whereas Na^{+} was comparable

Sample	Ca^{2+}		Mg^{2+}		Na^{+}	
	Calculated	PHREEQC	Calculated	PHREEQC	Calculated	PHREEQC
Unaffected Soil	0.58	0.34	0.58	0.39	0.87	0.83
Saline Soil	0.31	0.12	0.31	0.16	0.74	0.65

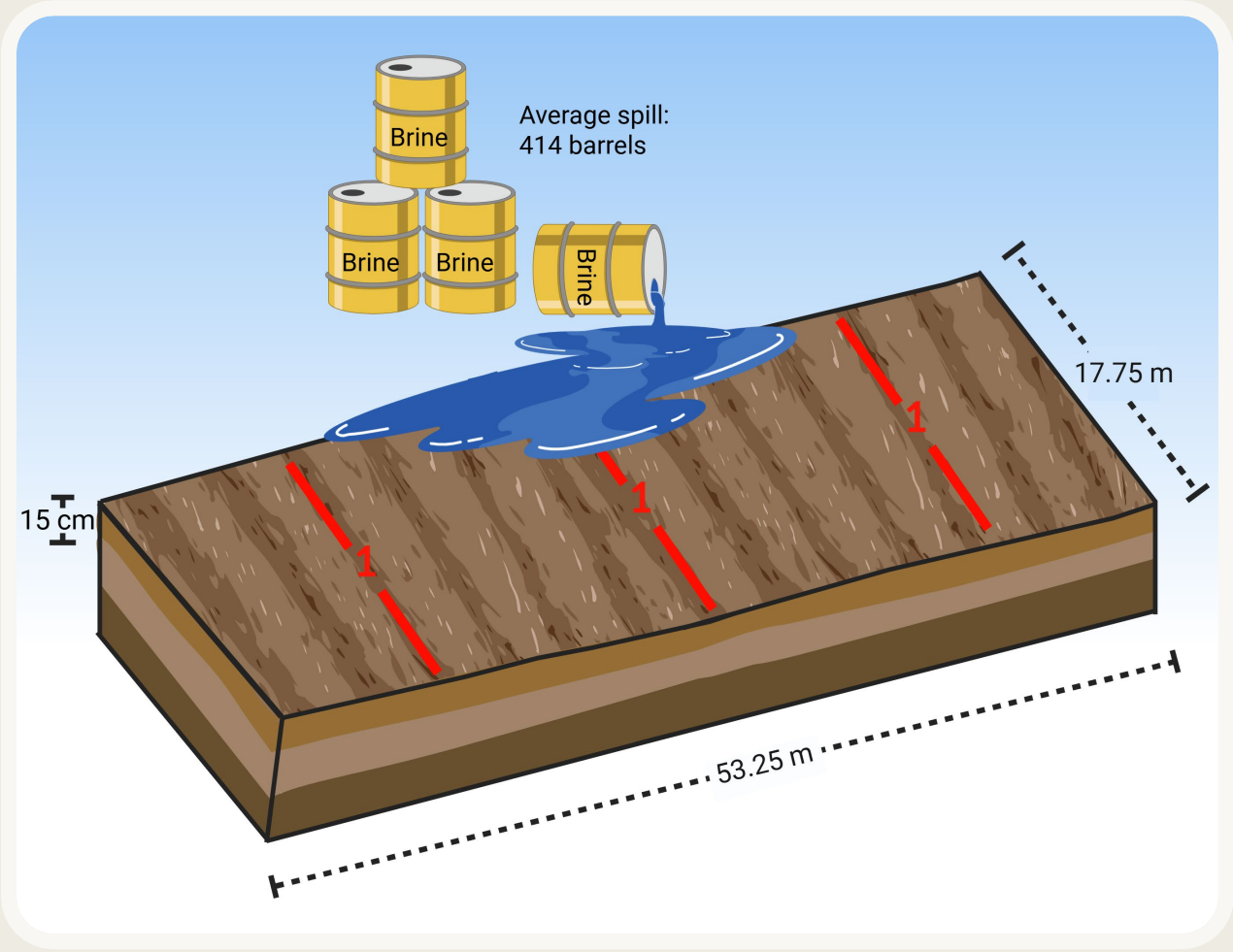
Saturation Indices

- Most saturation indices calculated by PHREEQC followed the same general trend as those calculated by the original authors
- Only calcite differed, but the authors stated that saturation indices close to zero in either direction may still represent mineral saturation/undersaturation as a result of sampling error

Sample	Gypsum SI		Calcite SI	
	Calculated	PHREEQC	Calculated	PHREEQC
Unaffected Soil	-0.59	-0.16	0.29	-0.62
Saline Soil	0.05	0.37	0.20	0.72

Part 2: Unaffected soil mixed with Produced water

Mixing Assumptions



Pore Space

- Sandy loam with a bulk density of 1.4 g/cm^3
- Pore Space = 1 - (1.4 / 2.65) = 47%
- Field capacity water filled pore space = 23.5%

Groundwater

- 15 cm soil depth x 23.5% = 3.53 cm water
- 0.0353 m x 53.25 m x 17.75 m = 33.37 m^3
- 33,370 liters of groundwater

Produced Water

- Average spill volume of 413.6 barrels or 65,757 liters

Water Ratios for Modeling

- 34% groundwater to 66% produced water
- Saturated paste extract = 2 × field capacity
- Final mix: 20% unaffected soil to 80% produced water

PHREEQC Inputs

Produced Water Sample

```
TITLE Mertz Project, part C.--Speciation via sample of
Produced Water.
SOLUTION 3  Produced Water
    temp      25
    pH        5.98
    units     mg/kgw
    density   1
    Alkalinity 141
    B         186
    Ba        4.85
    C(4)      173
    Ca        8420
    Cl        139000
    Fe        61.1
    K         3450
    Mg        1140
    Mn        3.55
    Na        83900
    Sr        404
    -water    1 # kg

SAVE solution 3
END
```

Unaffected Soil

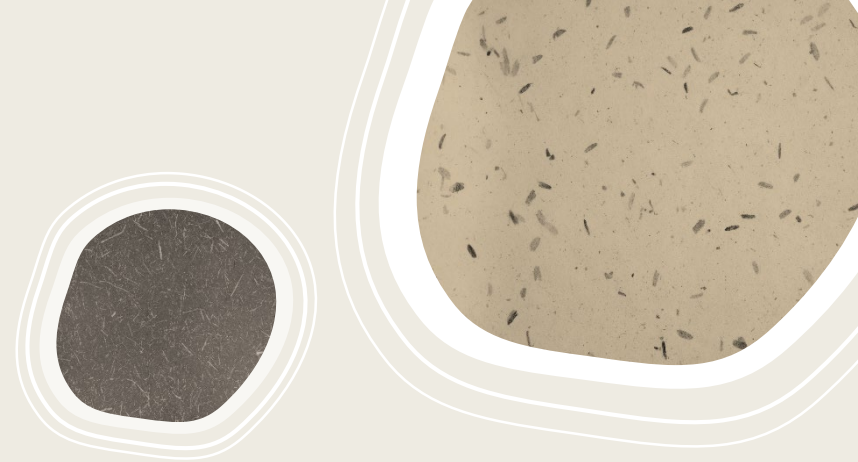
```
TITLE Mertz Project, part A.--Speciation via Saturated Extract
of Unaffected Soil.
SOLUTION 1  Unaffected Soil
    temp      25
    pH        6.5
    units     mmol/kgw
    density   1
    C(4)      3.3
    Ca        11
    Cl        2.9
    K         1.4
    Mg        4.9
    Na        4
    S(6)      15
    -water    1 # kg

SAVE solution 1
END
```

Mix

```
TITLE Mertz Project, part D.--Mix 20% Unaffected Soil
extract, 80% Produced water.
MIX
        1      0.20
        3      0.80
SAVE solution   4
END
```

SAR & Electrical Conductivity



- Sodium adsorption ratio quantifies sodium in the soil solution, not on the actual exchange sites
- $SAR = \frac{[Na^+]}{\sqrt{[Ca^{2+}]+[Mg^{2+}]}}$
- [ ] = concentration in mmoles/liter
- Used to determine whether soil is at risk of dispersing
- Dispersion is likely if the SAR:EC ratio is greater than 5:1

Sample	Electrical Conductivity	SAR
	dS/m	
Unaffected Soil	1.8	1.0
Saline Soil	12.0	11.5
Produced Water	207.0	227.7
Produced Mixed with Unaffected	114.0	202.1

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Photo References

(All other images are my own)

Saline Satellite Image

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Black & White Saline Seep Graphic

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ECe and SAR Graph & Produced Water Spills Affected Soil Photo

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Hettinger County, ND Map

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Thank You!

Please reach out with any questions

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