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2015

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Geology and Geological
Engineering

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B.S. in Environmental Geoscience
Senior Thesis

**BRINE SPILL REMEDIATION:
CRESTWOOD PIPELINE,
MCKENZIE COUNTY, NORTH
DAKOTA**

Abstract

Electrical Conductivity (EC) analyses of soil samples collected at a coproduced brine spill site near Mandaree, McKenzie County, North Dakota suggest that the site has been remediated. Five soil samples were taken from the area 12 inches below the ground surface. In the lab the saturation extract (Rhoades, 1982) method was used to collect a solution from the soil sample. From the solution we measured the EC. EC values showed a slightly higher reading from the samples within the spill site compared to sample that was taken outside of the spill where no contaminated was found. Chemical analyses of the water samples also indicate that the levels of sodium (Na) were slightly higher within the spill site. Although these measurements were higher within the spill site they're not high enough to present a salinity hazard.

Introduction

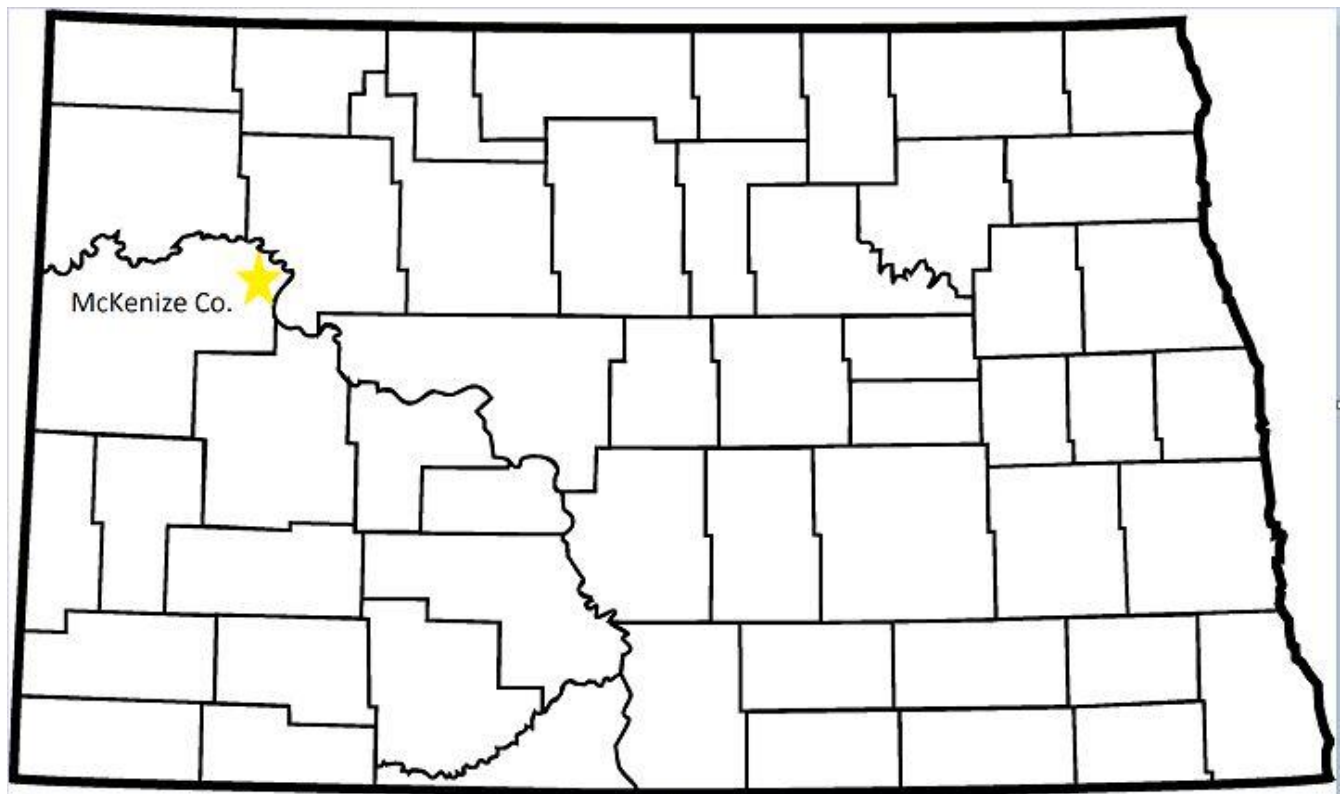
North Dakota has been in an economic boom due the increasing amount of oil production within the state. In 2013, North Dakota was the second largest oil producing state in the nation (U.S. Energy Information Administration, 2014). The driving factor behind the increasing amounts of oil production is hydraulic fracturing, better known as fracking, an oil recovery method that is being used worldwide. This method is used in a shale reservoirs to help with the permeability of the bedrock to help with the flow of oil. Hydraulic fracturing greatly increases the amount of oil that can be produced, but also releases large amounts of co-produced brine and fracking fluid.

Once a well begins operating, produced saline water (brine) along with oil and/or natural gas flows from the borehole. The brine is separated from hydrocarbons at the surface, and then produced water is trucked or piped away for disposal (Song, 2014). Pipelines require

maintenance, and inspection schedules have not always been adequate to prevent ruptures from spewing waste for days at a time. When spills occur, are they being remediated properly?

In July of 2014, a million gallons of coproduced brine and fracking fluid spilled from a broken pipeline onto a hillside just outside of Mandaree, North Dakota on the Fort Berthold Indian Reservation (Wood, 2014). The brine spill went undetected from July 4 through July 8. In that location brine made a path of dead vegetation, grass, brush, and trees. The path was about 8,240 feet long, which led down the hill into the Bear Den Bay, which flows into Lake Sakakawea that provides drinking water to the Indian Reservation, but an unknown amount of salt water may have entered Bear Den Bay (Wood, 2014).

Figure 1. McKenzie County, North Dakota. The yellow star indicates the study area.



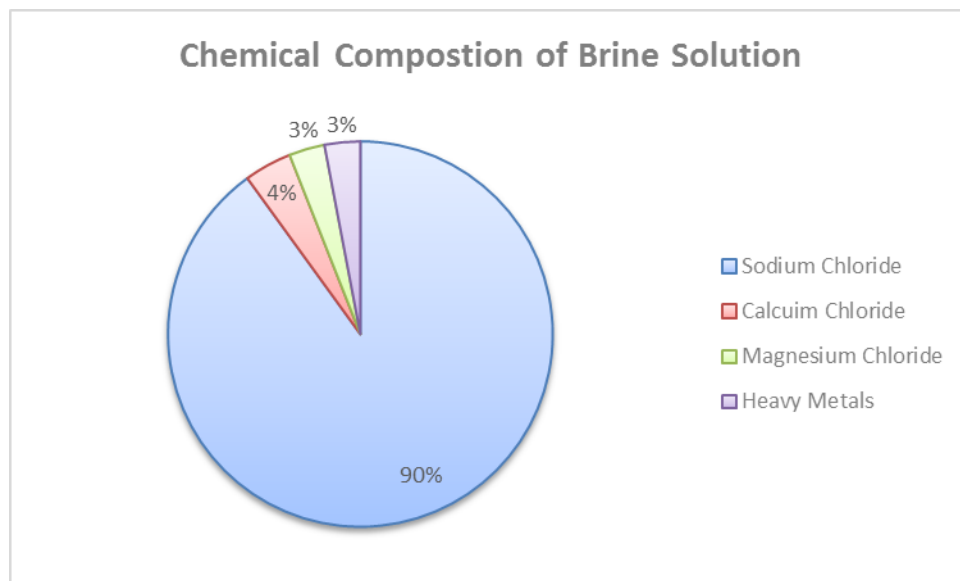
Background

Brine Composition

Oil companies commonly refer to coproduced water and coproduced water with fracking fluid as salt water (Song, 2014). In this paper I will refer to these waters as brine.

These brines are highly saline waters that come from the fracked shale rock formation of the Williston basin, thousands of feet below Earth's surface. The brine is five to eight times saltier than ocean water (Wood, 2014). North Dakota brine consists of 90% sodium chloride (NaCl) (see Figure 2). A thousand gallons of brine contains over a ton of NaCl (Doll, 1989). The other ten percent of the mixture consists of calcium chloride (CaCl₂), magnesium chloride (MgCl₂), and assorted heavy metals. These heavy metals consist of cobalt, nickel, copper, zinc, arsenic, selenium, silver, cadmium, antimony, mercury, thallium, and lead. Other dissolved substances include barium, and bromide (Song, 2014).

Figure 2. Chemical Composition of North Dakota Brine (Doll, 1989)



Site Remediation

North Dakota regulation requires brine spills to be reported to the North Dakota Environmental Health Service. The company at fault is responsible to ensure that the contamination is cleaned up. (North Dakota EHS, 2014). Every contractor has their own way of remediating these sites, from removing all the contaminated soil to spraying water on the site

At Mandaree, they took several steps to remediate this one million gallon spill site. A dam was built between Bear Den Bay and Lake Sakakawea to keep brine from flowing into the lake. A berm was built around the contaminated area to contain the spill. Tanker trucks came into the spill site and vacuumed all the standing water (Wood, 2014).

Finally, the primary goal in site remediation is to reduce the amount of soil dispersion. In a non-dispersive soil, clay platelets are flocculated and held together by calcium ions. When large amounts of sodium are introduced, sodium displaces calcium and the clay particles disaggregate. Reorganization of clay platelets closes off soil porosity, resulting in poor rain and meltwater infiltration and eventually gulling. Gypsum is applied to the sodic soil to provide a source of calcium to displace the sodium, reducing dispersion (Sublette, n.d.).

Objective

The purpose of this study was to see how well the Crestwood pipeline brine spill remediated? Can salts can still be detected in the soils at the site?

Methods

Field work was conducted on May 24, 2015 in McKenzie County. Soil samples were retrieved from five different locations, one from above the spill site and four within the spill area (Figure 3). Each soil sample was taken 12 inches below the surface, placed in a Ziploc bag and stored in cooler to prevent samples from dehydrating.

Figure 3. Sample names and location within the study site. Crestwood Pipeline in the blue with the area of pipeline rupture in red.



As of May 24, 2015, the vegetation of the study site was in poor condition. Some areas within the site had little vegetation, and some areas where the samples were retrieved had dead vegetation as seen in Fig 4-6. Where the water drains into Bear Den Bay, the water seemed to have a film over it; that's where I took sample #4 near the water from (Figure 7).

Figure 4. The location from where Roadside sample was retrieved (Photo by: Jeannotte 2015).



Figure 5. The location from where Hill within the spill sample was retrieved (Photo by: Jeannotte 2015).



Figure 6. The location where sample Hill above the water was retrieved from (Photo by: Jeannotte 2015)



Figure 7. The location from where the near the water sample was retrieved. There was a film over the water in this location (Photo by: Jeannotte 2015).



Lab work was conducted during May 26 - 27 2015 at the Turtle Mountain Community College in Belcourt North Dakota. Saturation Extraction Method (Rhoades, 1982) steps are as follows:

1. Weigh out 250 grams of soil, bake the sample in an oven at a temperature of 180°F for 30 minutes to find the water percentage of the soil (Below is an example of how to calculate the water percent in the soil.)

$$\frac{250 - 218.43}{250} * 100 = 12.63\%$$

2. Using a mortar and pestle, the baked soils were crushed into fine powders.
3. Add a sufficient amount of deionized water while mixing to saturate the soil into a soil paste. For each soil sample, the amount of water added was different as shown in Table 1.
4. Cover the resulting paste and allow to sit overnight.

Table 1. *The weight of the soil before and after it was baked, water content within the soil, and the amount of deionized water to create a paste.*

	Oven Baked			Deionized H2O to Create Paste (ml)
	Weight Before (g)	Weight After (g)	Water Percentage	
Uncontaminated (control)	250 g	218.43 g	12.63%	100 ml
Road side #1	250 g	201.31 g	19.48%	114 ml
Hill-W/in Spill#2	250 g	200.10 g	19.96%	111 ml
Hill by the Water #3	250 g	197.96 g	20.82%	110 ml
Near the Water #4	250 g	194.6 g	22.16%	161 ml

5. Filter the liquid from the paste using a Buchner funnel fitted with highly retentive filter paper. Each sample took about 45 minutes to become fully dry.

Since NaCl makes up 90% of the dissolved substances in the brine solution, I find it necessary to compare the levels of salinity from within the spill site to those directly above the spill site on the hill where no brine was reported. There are several ways to measure salinity, but an inexpensive way is to measure the electrical conductivity (EC) of the soil samples. EC is a measure of how well a material conducts an electric charge. Although EC is a good method of indicating salinity, it doesn't identify the ions in solution.

To determine the Na and Ca ions within the solution the Atomic Absorption Spectrometry (AAS) equipment was used. When using the AAS, standards have to be made for all of the metals of interest. Six standards were made for the Na ions. Four standards were made for the Ca ions (Table 2). The AAS has other guidelines, like wavelengths and slits for every metal. For Na, the wavelength is set at 589 nanometers and at a slit of 0.2 and for Ca the wavelength is 422.7 and at a slit of 0.7. Once these guidelines are met then the standards and the samples are sent through the AAS.

2. Atomic absorption of the created standards of Na and Ca ions.

Created Standards for Na		Created Standards for Ca	
stand conc ppm	stand abs	stand conc ppm	stand abs
0.25	0.031	0.625	0.002
0.68	0.055	2.5	0.01
1	0.064	5	0.02
2	0.104	10	0.038
4	0.167		
8	0.211		

Results

After doing the lab work, the electrical conductivity of the different samples within the spill site and the sample away from the spill site doesn't vary much as shown in Table 3. Micro-Siemens/centimeter is the units of the electrical conductivity for a water sample. Soil electrical conductivity is measured in deci-Siemens/meter. Electrical conductivity ranges from 0.989 ds/m, which is the uncontaminated sample to the highest reading 1.043 ds/m and which was within the spill site on top of a hill. The elevated levels in electrical conductivity suggest that the salt water spill was remediated but isn't quite back to the pre-spill levels, which is seen in the control sample's level at 0.989 ds/m. The electrical conductivity levels found in this remediated spill site are not considered to be a salinity hazard. According to the United States Department of Agriculture, non-saline soil has electrical conductivities of 2 ds/m or less (Richards, 1954). My results show that the levels of electrical conductivities within the site are well below 2 ds/m.

Table 3. *Electrical Conductivity of the soil samples.*

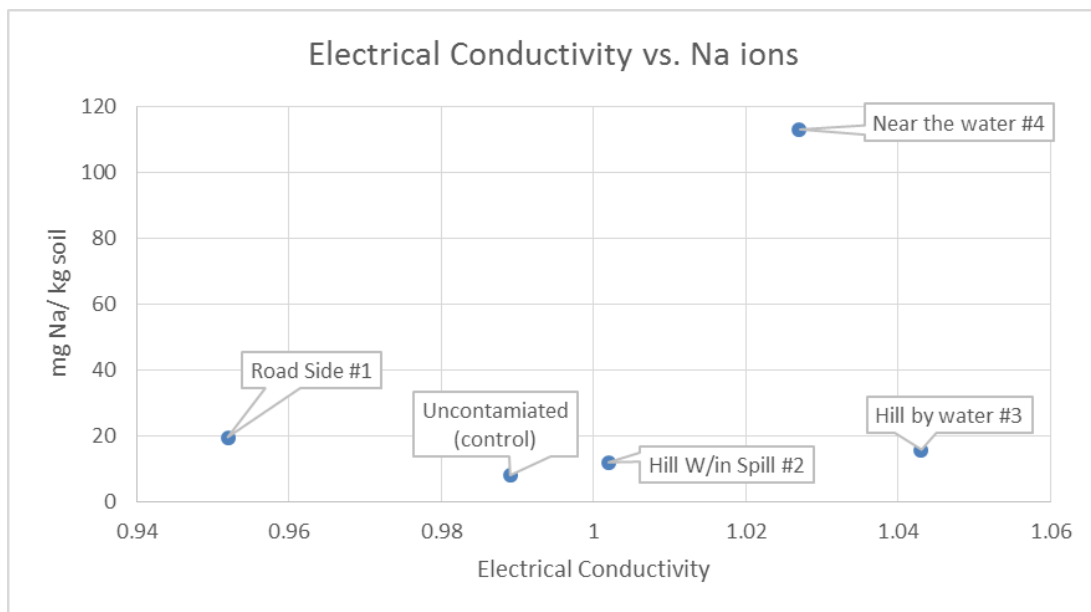
	Electrical Conductivity	
	micro-Siemens/centimeter	deci-Siemens/meter
Uncontaminated (control)	989.5 $\mu\text{s/cm}$	0.989 ds/m
Road side #1	952.7 $\mu\text{s/cm}$	0.952 ds/m
Hill-W/in Spill#2	1002.5 $\mu\text{s/cm}$	1.002 ds/m
Hill by Water #3	1043.8 $\mu\text{s/cm}$	1.043 ds/m
Near the Water #4	1027.9 $\mu\text{s/cm}$	1.027 ds/m

After sending our samples through the AAS we find the different amounts of Na and Ca within our samples. The amount of Na in the samples should correspond with the EC measurements that were taken. Unfortunately, the amount of Na ions don't correspond to EC measurements (Table 4). The reason these values don't correspond is due to the different impurities in the soil that weren't accounted for. Natural impurities within the soils can distort the levels of EC (Gawel, n.d.). The amount of Ca found vary at different amount throughout the site. This might be a result of the different amounts of gypsum that was placed on the site.

Table 4. *The amount of Na and Ca ions found within the samples.*

	EC ds/m	mg Na/kg soil	mg Ca/kg soil
Uncontaminated (control)	0.989	7.9	23.2
Road side #1	0.952	19.3	23.2
Hill W/in Spill #2	1.002	12	9.4
Hill by water #3	1.043	15.7	59.7
Near the water #4	1.027	113.2	44.7

Figure 8. The difference between the Electrical Conductivity and Na ions.



Conclusion

In conclusion, after completing my research and finding my results, I conclude that the Crestwood Brine spill in McKenzie County, North Dakota, has been remediated to the point where these soils are not considered to have a saline hazard (Richards, 1954). Salinity may be remediated in the top 12 inches of soil, but contaminants may be located further below the surface. We do not know whether these brines waters are still flowing within the ground, making their way in to our ground water, and if they may cause problems when they reappear in the future.

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