

Produced Water Spills Related to Unconventional Oil and Gas
Development in North Dakota

By

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Abstract

Beginning in 2007 unconventional oil production increased dramatically in the region of North Dakota overlying the Bakken shale formation. Since, the North Dakota Department of Health has reported more than 4,000 accidental spills of produced water. Our study seeks to follow up on a 2016 study by Nancy Lauer et al., which characterized the major and trace element chemistry of 29 surface waters in areas impacted by oil and gas wastewater spills. Comparing to background levels and the composition of Bakken produced waters, we used conservative element chemistry characterized 33 surface water samples sites impacted or potentially impacted by produced water spills, including 6 sites sampled the year before. Soil and sediment collected from the sites analyzed for total radium activities (^{228}Ra & ^{226}Ra) showed persistent contamination. One of the most heavily affected sites, an 11 million gallon spill near Blacktail Creek, that was characterized the year before experienced extensive remediation and displayed much lower levels of contaminants in 2016. However, this site was an anomaly; other sites continue to display persistent inorganic contamination up to 5 years after the initial spill.

Executive Summary

Unconventional oil and gas development in the Bakken region of North Dakota has increased dramatically since 2007 when hydraulic fracturing and horizontal drilling techniques made it more economically efficient to develop. The water produced by this process is extremely saline and contains high amounts of trace metals and naturally occurring radioactive material that can contaminate surface water resources and persist in the environment.

This study seeks to expand upon a 2016 study conducted by Nancy Lauer et al. that characterized the major ion and trace element chemistry of 29 surface waters impacted by produced water spills in the Bakken. That study established geochemical and isotope tracers specific to brines in the region to identify produced water spills in the environment. In addition to high dissolved salt concentrations and other trace metals and contaminants, produced water contain elevated amounts of radium(^{226}Ra & ^{228}Ra) that can accumulate and be measured in the sediments and soils of impacted sites.

The introduction section of this report presents the issues facing the Bakken region of North Dakota, and provides a brief overview of the region's background and produced water chemistry.

The methods section of this study outlines the sampling frame and overview of site selection, defines sampling protocols, and explains how data was analyzed.

The results section has four defined segments. The first outlines how major ion/conservative chemistry relationships can characterize sample sites into two types of impacted sites and background sites. Next, a discussion of the persistent salt and trace metal contamination, comparing sites sampled in both 2015 and 2016. The third segment of results focuses on high activity levels of naturally occurring radioactive matter in Bakken produced water and impacted site sediments and soils. Last, this study revisits the site of North Dakota's largest spill in history, the remediation process, and how successful the remediation was.

The final section outlines the environmental and health implications of persistent surface water contamination by produced water and makes recommendations for the focus of future potential studies.

This report makes several key points and recommendations:

- Impacted surface waters can be categorized using conservative element chemistry and relevant relationships.
- Sites revisited in this study displayed persistent levels of salt and trace metal contamination characteristic of surface waters impacted by brines.
- Produced waters contain high levels of long-lived naturally occurring radioactive materials that can precipitate and adsorb to sediments and minerals.
- Appropriate and extensive site remediation can reduce contamination at even the most heavily impacted sites.

I. Introduction

North Dakota currently contains the second largest crude oil reserves in the nation.¹ Advances in drilling technology, namely hydraulic fracturing and horizontal drilling, allowed for the exploitation of the Bakken formation in the Williston Basin underlying western North Dakota and parts of South Dakota, Montana, and Canada. Large-scale oil production from North Dakota and Bakken counties exponentially grew from approximately 150 thousand barrels per day in April 2007 to surpass 1 million barrels in April 2014.² To facilitate this exponential rise in production, infrastructure development has also intensified in the Bakken region. According to the 2014 Baker and Hughes well count data, there were an estimated 9704 unconventional wells in the region that have produced an estimated total 31.4 billion gallons (118.9 billion Liters) of oil and gas produced water.³ Produced water yield in the Bakken is far greater than other shale plays; first year well totals alone were comparable to four year totals in the Barnett, Denver, and Marcellus Basins.¹⁵

Produced water composition is complex and includes the naturally occurring hypersaline formation water, oil, hydrocarbon condensates, and small percentage of the added organic chemicals that are injected for the fracturing process.⁴ Produced waters are also known to contain high amounts of trace metals including high concentrations of Strontium, Boron, and Manganese.⁵ Similarly, naturally occurring radioactive materials(NORM) that were trapped within formations like the Bakken are released and return to the surface with the produced water.⁶ If these contaminants are released to the environment at elevated concentrations they can harm local water quality and threaten ecological health.⁷ Several studies show the release of produced water to the environment from unconventional oil and gas development can threaten nearby surface and groundwater quality through a variety of releases including: effluents to local

streams and rivers following inadequate treatment by water treatment facilities,^{4,8,9} application to roads and fields as deicing agents and dust suppressants,¹⁰ leaks and spills from pipelines, disposal sites, and trucks,^{5,11} as well as illegal dumping¹³. Once released to the environment, produced water has been shown to contaminate local surface water, shallow groundwater, and stream sediments with high levels of salinity, trace metals, and NORM.^{4-9,11}

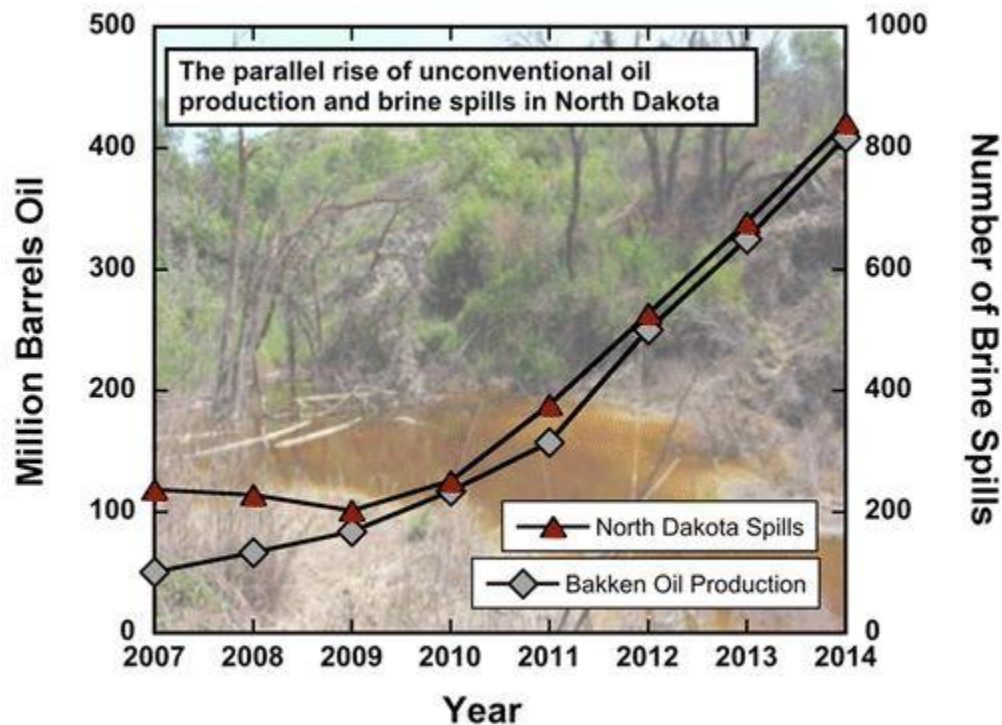


Figure 1. Graph showing how oil production in Millions of barrels mirrors the number of produced water spills in North Dakota from 2007 to 2014. Spill data sourced from the North Dakota Department of Health.¹² Oil production data for the Bakken region collected from the Energy Information Administration.² Figure taken from Lauer et.al. 2016.⁵

As production and unconventional oil development have increased in the Bakken region, so have the produced water spills. From 2007 to when production peaked in 2014 there were approximately 3,900 brine spills reported to the North Dakota Department of Health (NDDH) by well operators (Figure 1).⁵ The NDDH defines a brine spill as an accidental release of produced water that has the potential to impact nearby surface water or groundwater. Spills associated

with unconventional oil production continue to occur however, as over the past twelve months there have been 1,003 spills contained within the boundaries of the production or exploration facility, and another 305 that were not contained, i.e. an overflow of the facility boundaries or a pipeline leak.¹² Produced water is almost exclusively disposed of in North Dakota through deep well injection. Spills often can occur during the transport of the brine via pipelines, tanker truck transport, or during the filling or emptying of on-site storage tanks. The Bakken region is unlike many other oil-producing regions, such as the Barnett region of Texas, because it did not experience heavy development for conventional oil and gas prior to the unconventional exploration. Regions that have experienced historical conventional oil and gas production have a legacy of contamination that is unseen in the Bakken region, ensuring that the produced water spills are associated with the recent increase in unconventional production.

Studies focusing on the Bakken region have increased significantly since 2014, the time of peak production. The USGS conducted two recent studies in the region. A 2016 study assessing the effects of the Blacktail Creek spill at two different time points, February and June 2015, found elevated salts (Na, Cl, Br), trace metals (Sr, B, Li), ammonium, and hydro carbons in the creek at the spill site.¹⁴ The study also found elevated levels of the trace metals B and Sr, and Radium activities up to fifteen times the background concentrations downstream from the site. Biological impacts on the aquatic ecosystem were also present with reduced fish survival and estrogenic inhibition at downstream sites. An earlier 2014 USGS study assessed forty-eight surface and shallow groundwater samples at three study sites near oil and gas production in the region finding that thirty-four were moderately to extremely contaminated with brine, with another seven potentially contaminated.¹³ The study hypothesized that some of the salinity in the sites came from buried reserve pits installed in the late 1960's, showing that contamination can

persist in aquatic resources for up to four to five decades. The study also found that Brine is capable of lateral groundwater migration of distances up to 800m over twenty years depending on the type of near surface sediments.¹³ Another retrospective case study in the Bakken region conducted by the EPA showed that a well pad blowout contaminated nearby shallow groundwater wells with brine and hydrocarbons.¹⁶

Surface and groundwater in North Dakota has a unique chemical make-up that makes identification of impacted waters complicated. North Dakota streams and surface water are naturally saline with the dominant cations: calcium, magnesium, potassium, and sodium. The dominant anions for the majority of the surface waters are sulfate and bicarbonate, with only a small fraction dominated by chloride.¹³ Bakken produced water has been shown to be primarily dominated by the solutes chloride, calcium, sodium, and bromide, while containing high amounts of trace metals including strontium, boron, manganese, nickel, cadmium, copper, zinc, barium, lead, radium and ammonium.^{13,17,5} This key difference in major solute composition makes it possible to identify spills without relying solely on discerning whether the salinity is natural or originating from produced water.

This study seeks to follow-up and expand upon the work by Lauer et al. 2016.⁵ That study characterized twenty-nine surface water samples, four Bakken produced water samples, and thirty-seven grab sediment and soil samples from the Bakken region collected in July 2015. They confirmed that background waters were highly saline and dominated by sodium, sulfate and bicarbonate, had high pH ranging up to 9.3, high total organic carbon (TOC), low chloride, and high bromide to chloride ratios. Surface water samples were characterized into three categories: type A spills were of larger volumes with composition indicating mixing with saline background water, type B spills were smaller and isolated likely leading to evaporation and

precipitation of minerals, and background waters. Spills were identified and categorized by solute ratios and stable isotope composition and ratios. Lauer et al. also found that impacted site sediments contained elevated levels of NORM focusing on persistent radium isotopes ^{228}Ra ($t_{1/2} = 5.75$ years) and ^{226}Ra ($t_{1/2} = 1600$ years). The results from this study indicated that there were negative environmental implications for impacted surface waters, and that the resulting contamination would likely persist for many years after the initial spill. Here, we attempt to determine the persistence of contamination at some of the most heavily impacted sites characterized by Lauer et al., to identify and characterize any new impacted surface waters, and to analyze and explain any new and unexpected contaminants that may be naturally occurring.

II. Materials and Methods

A. Sampling Overview: We collected thirty-seven water samples, thirty-three from surface water and four groundwater, and twenty-two grab sediment and soil samples from the Bakken region of Western North Dakota in June 2016 (Figure 2). Additional sample information, locations and site description provided in Appendix (Figures A1 and A2, Table A1). The July 2015 sampling campaign identified four reported surface water sites heavily impacted by produced water from unconventional oil and gas production. These characterized spills included North Dakota's largest spill events on record, the Blacktail Creek Spill Site (In 2015 referred to as ND123 and ND 126, here as ND219, ND 220, ND221, and ND222), and the Bear Den Bay Spill (ND102, ND103, and here as ND206, ND207, and ND 208). The Blacktail Creek spill was the site of the single largest spill in North Dakota history releasing an estimated 11 million liters of brine from a pipeline into the nearby creek in January 2015. Blacktail Creek is a tributary to the Little Muddy River, which flows into the Missouri River. The Bear Den Bay Spill was a July 2014 underground pipeline leak that spilled an estimated 3.8 million liters of produced water

down a ravine to collect in Bear Den Bay, which is located approximately 0.4 km upstream of Lake Sakakawea and the drinking water intake for the Fort Berthold Indian Reservation. Two other spill sites targeted for re-characterization were surface waters impacted by smaller spills. One site (ND129, here as ND 210) estimated to be a brine spill of about 48,000 liters occurred in July 2011, the other site (ND113, here as ND226) was a spill of an unknown quantity or date. Other sites sampled were from potentially impacted surface waters and groundwater wells selected for their proximity to well pads or disposal sites for produced water. We included several sample sites for characterization to provide background levels of constituents for the area for comparative purposes.

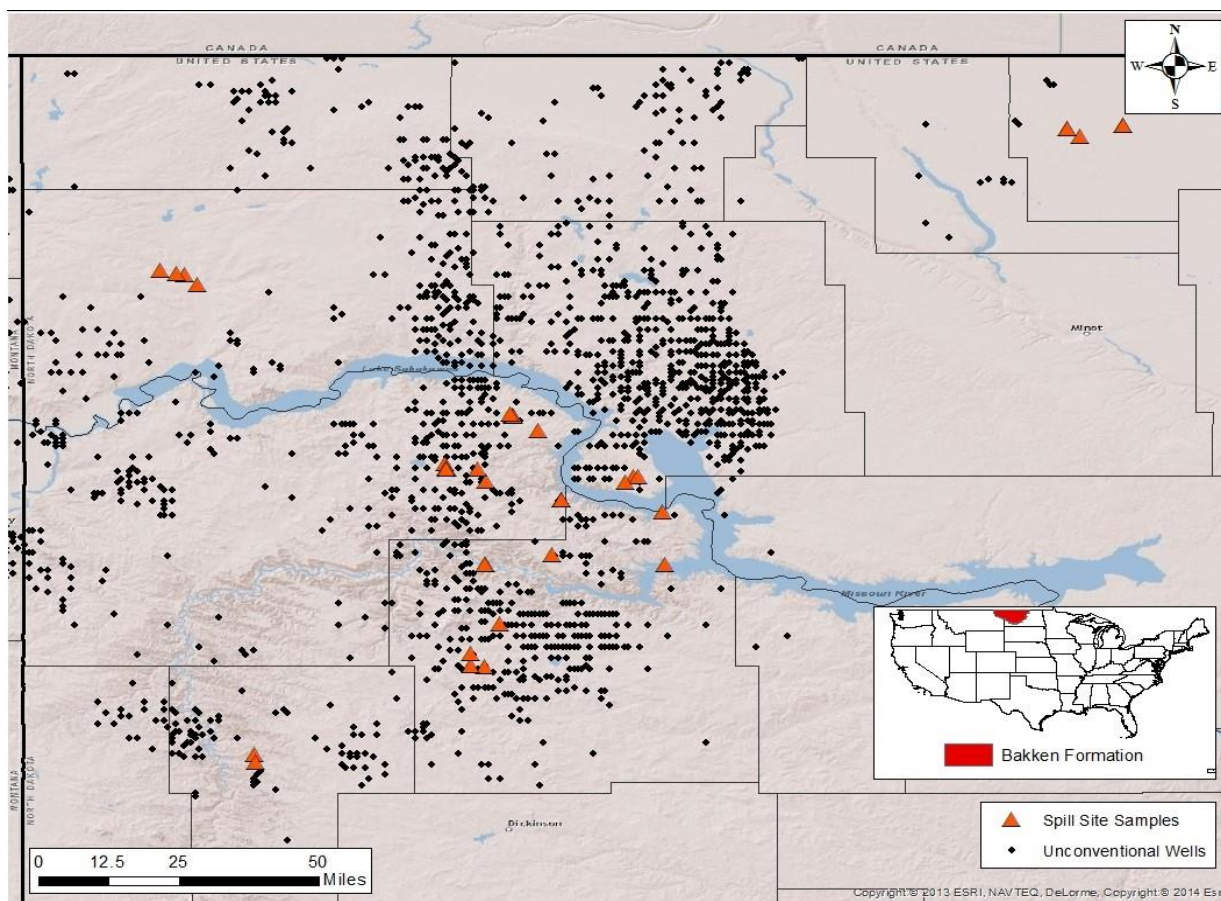


Figure 2. Map of the Bakken region of Western North Dakota depicting the locations of unconventional oil well pads as of 2014 and sampling sites used for this study. Location and number of well pads taken from Kondash et al. 2015.³ Observe the relationship between well pad density and spill sites sampled.

B. Sample Collection Protocols: We collected water samples from June 18-June 24, 2016. Characterization of collected samples through analysis of major anions, major cations, trace metals, alkalinity, total organic carbon, and radium yielded site profiles for identification of spills and for comparison to 2015 sites. We wore new gloves for all sample collection. Alkalinity sampling occurred by fully submerging a new 60 ml high-density polyethylene (HDPE) bottle and capping it under water to ensure zero headspace. For major cation and trace metals, we used an acid washed 60 ml HDPE bottle containing a preservative 10% nitric acid to collect the sample after filtering it through a 0.45- μm syringe filter to remove any particulates. We collected samples for dissolved organic carbon and major anion analysis in 60 ml HDPE bottles after using a 0.45- μm syringe filter. Samples were stored in coolers on ice immediately following collection until they could be stored in a refrigerator in the laboratory before analysis. We collected sediment/soil samples from select sites for Radium analysis using a water rinsed spade to scoop the grab samples into plastic jars.

C. Data Analysis: We determined alkalinity for the samples by titrating the sample down to pH 4.5 with 0.2 M hydrochloric acid. Major cation concentration was measured by direct current plasma optical emission spectrometry (DCP-OES). For trace element analysis, we employed a VG PlasmaQuad-3 inductively coupled plasma mass spectrometer (ICP-MS). A Thermo Fisher Dionex measured major anion constituents by ion chromatography (IC). A Shimadzu TOC-V CPH total carbon analyzer provided total organic carbon measurements. For Nitrate and ammonium analysis flow injection analysis(FIA) on a Hach Lachat provided concentrations.

Measuring Radium isotopes (^{226}Ra and ^{228}Ra) from grab sediment and soil samples was conducted at the Duke University Laboratory for Environmental Analysis of Radionuclides (LEARN). The LEARN lab uses a Canberra broad energy germanium gamma detector that is

calibrated with a standard reference ore (DL-1a). Prior to analysis soil and sediment samples are oven dried, pulverized with mortar and pestle, packed into 40 mL petri dishes, tightly wrapped in electrical tape, and then coated in wax to ensure limited escape of gaseous Radon (^{222}Rn $t_{1/2}=3.8$ days). Then the samples are incubated for at least three weeks to allow for radioactive secular equilibrium between ^{226}Ra and its short-lived daughter ^{214}Pb ($t_{1/2}=27$ min). ^{226}Ra activity was measured through the ^{214}Pb peak at 351 kEv, and ^{228}Ra activity through the ^{228}Ac peak at 911 kEv. Samples were left on the gamma detector for 12-48 hours to account for statistical error, which averaged below five percent.

III. Results and Discussion

A. Characterization of Surface Water Samples: Samples were evaluated based on the chemical data, their major cation and anion concentrations, trace metal levels, and corresponding relationships. Following the categorization used by the previous study Lauer et al. 2016, samples were sorted into type A and type B sites impacted by spill waters, and background sites. In conjunction with previous studies of North Dakota surface waters, background waters were highly saline. Dominant anions were sulfate (avg 2,566.4 mg/L) and bicarbonate (avg 547.6 mg/L). Sodium (avg 678.7 mg/L), calcium (avg 174.2 mg/L), and magnesium (avg 146.8 mg/L) were the dominant cations (Table 1). Compared to type A, type B, and the Bakken produced waters background waters were low in chloride (avg 57.4 mg/L) and bromide (avg 0.3 mg/L) with a higher Br/Cl ratio (avg 8.02 E^{-3}). SO_4/Cl ratios were high as to be expected with the naturally high sulfate levels in North Dakota surface waters (avg 99.98), and helped to separate background samples from impacted sites. The salinity of Bakken region surface waters is believed to be derived from evapotranspirative concentration of groundwater high in sulfate and calcite, gypsum and mirabilite precipitation.¹⁸ Observed in Lauer et al., background HCO_3 was

again highly correlated with TOC concentrations, reaffirming the hypothesis that the background dissolved inorganic carbon is derived from organic matter oxidation (Figure A2).

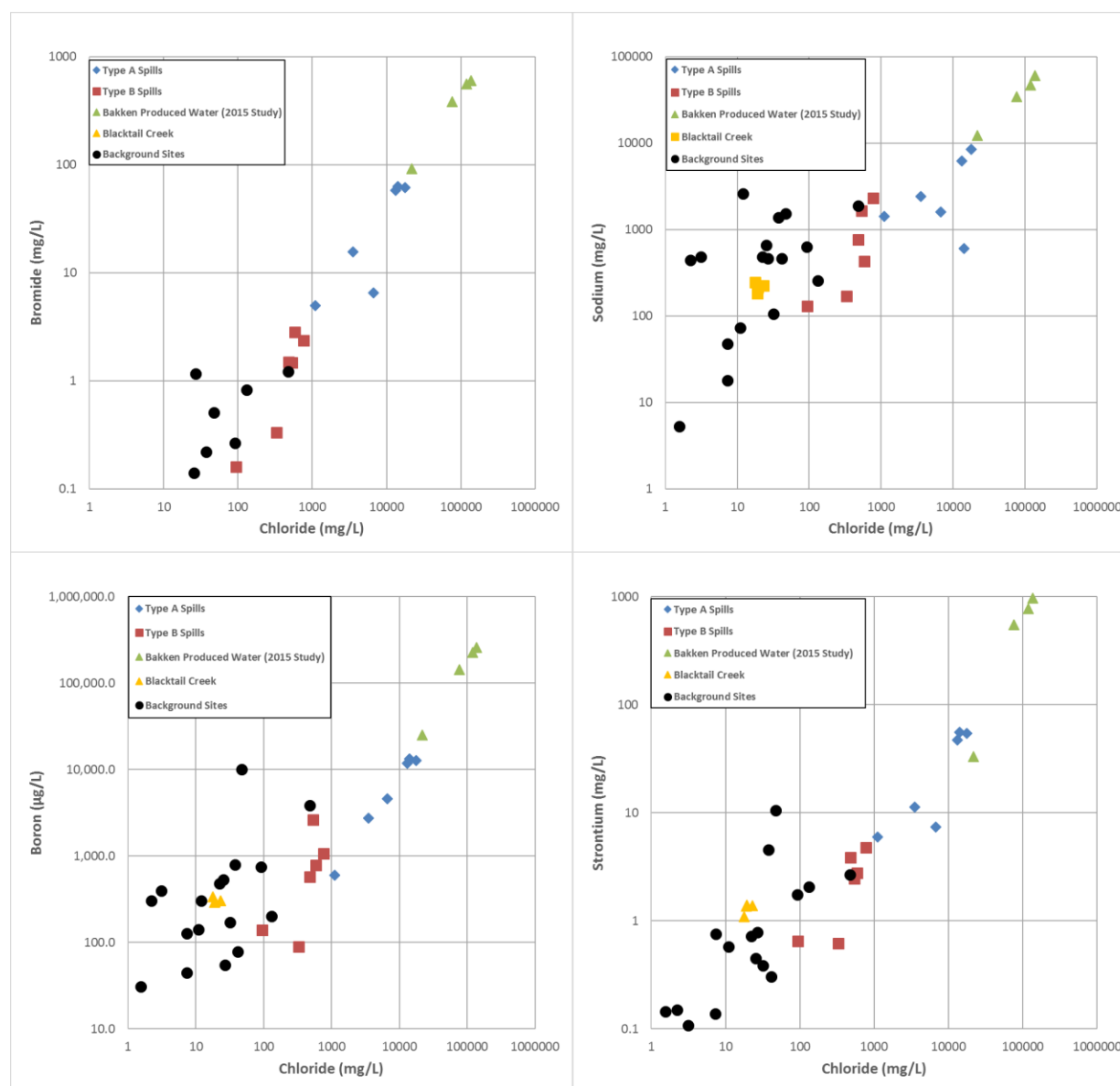


Figure 3. Bromide, sodium, boron, and strontium plotted against chloride concentrations for Type A, Type B, Bakken produced water samples, Blacktail Creek, and background sample sites. Type A spills closely resemble the Bakken produced waters supporting the Lauer et al. conclusion that there is a conservative mixing relationship between the produced water and the saline background waters. Note that the Blacktail Creek samples fall well within the background as opposed to their previous Type A classification.

Table 1. Characterization of Major Chemistry of Bakken Produced Waters, Spill Impacted Waters, and Background Waters

Sample ID	Sampled 2015 Y/N	Cl (mg/L)	Br (mg/L)	SO ₄ (mg/L)	HCO ₃ (mg/L)	Ca (mg/L)	Mg (mg/L)	Sr (mg/L)	Na (mg/L)	NH ₄ (mg/L)	TOC (mg/L)	Br/Cl	SO ₄ /Cl	B/Cl	Sr/Cl	Na/Cl
Type A Spills																
ND 206	Y	13,168.9	58.1	3,645.2	211.0	1,644.3	930.4	47.4	6,271.1	0.4	53.3	4.41E-03	2.77E-01	9.03E-01	2.88E+01	4.76E-01
ND 207	Y	14,226.4	63.2	2,372.2	292.0	205.3	726.0	55.9	604.2	1.4	45.855	4.44E-03	1.67E-01	9.31E-01	2.72E+02	4.25E-02
ND 208	Y	3,535.5	15.6	2,320.1	294.0	727.1	378.9	11.3	2,408.6	<0.01	54.2	4.42E-03	6.56E-01	7.77E-01	1.55E+01	6.81E-01
ND 226	Y	1,106.3	5.0	3,878.9	507.0	605.3	425.6	6.0	1,431.3	<0.01	65	4.49E-03	3.51E+00	5.38E-01	9.92E+00	1.29E+00
ND 210	Y	6,704.9	6.5	979.0	49.0	1,997.9	448.1	7.4	1,597.2	10.1	46.505	9.76E-04	1.46E-01	6.81E-01	3.71E+00	2.38E-01
ND 214	N	17,788.0	61.6	4,514.4	307.0	1,694.9	1,270.3	54.6	8,490.4	<0.01	31.695	3.46E-03	2.54E-01	7.15E-01	3.22E+01	4.77E-01
Average		9,965.0	40.7	3,346.2	322.2	975.4	746.2	35.0	3,841.1	0.9	49.4	4.24E-03	9.72E-01	7.73E-01	7.18E+01	5.94E-01
Type B Spills																
ND 209	Y	94.5	0.2	579.4	371.0	154.0	98.4	0.6	129.6	0.1	49.545	1.68E-03	6.13E+00	1.46E+00	4.20E+00	1.37E+00
ND 213	Y	329.6	0.3	469.7	443.0	159.6	135.0	0.6	170.5	<0.01	51.55	1.00E-03	1.42E+00	2.71E-01	3.86E+00	5.17E-01
ND 217	N	537.6	1.5	2,343.3	1,290.0	148.0	115.8	2.5	1,660.9	<0.01	82.7	2.74E-03	4.36E+00	4.88E+00	1.84E+01	2.62E+00
ND 218	N	770.6	2.4	4,540.2	820.0	212.2	243.0	4.8	2,332.3	<0.01	50.45	3.05E-03	5.89E+00	1.39E+00	2.46E+01	2.59E+00
ND 224	N	586.2	2.8	1,843.0	635.0	466.3	313.9	2.8	432.9	<0.01	26.57	4.80E-03	3.14E+00	1.33E+00	5.93E+00	7.39E-01
ND 231	N	481.5	1.5	2,334.7	48.0	328.0	182.9	3.8	765.5	<0.01	20.63	3.11E-03	4.85E+00	1.18E+00	1.17E+01	1.59E+00
Average		1,357.8	2.2	1,869.9	522.3	495.1	219.6	3.2	1,012.7	5.1	46.9	2.48E-03	3.71E+00	1.60E+00	1.03E+01	1.38E+00
Produced Water From 2015																
PW 1	-	119,989.0	558.0	128.0	35.0	12,033.0	1,001.0	774.0	47,217.0	2,110.0	134.3	4.65E-03	1.07E-03	1.88E+00	6.45E-03	3.94E-01
PW 2	-	75,892.0	384.0	102.0	169.0	8,573.0	741.0	551.0	34,745.0	1,200.0	166.3	5.06E-03	1.34E-03	1.88E+00	7.26E-03	4.58E-01
PW 3	-	21,728.0	91.6	0.0	856.0	372.0	118.0	33.1	12,271.0	44.8	1080	4.22E-03	0.00E+00	1.15E+00	1.52E-03	5.65E-01
PW 4	-	136,220.0	601.0	293.0		15,346.0	1,299.0	970.0	60,571.0	2,520.0	144.9	4.41E-03	2.15E-03	1.91E+00	7.12E-03	4.45E-01
Average		88,457.3	408.7	130.8	353.3	9,081.0	789.8	582.0	38,701.0	1,468.7	381.4	4.58E-03	1.14E-03	1.70E+00	5.59E-03	4.65E-01
Blacktail Creek																
ND 219	Y	23.0	0.1	1,025.1	363.0	138.9	162.2	1.4	223.7	<0.01	26.465	3.28E-03	4.45E+01	1.32E+01	9.97E+00	9.72E+00
ND 220	Y	19.3	0.1	1,051.1	368.0	143.8	171.7	1.4	214.9	<0.01	25.29	4.30E-03	5.44E+01	1.53E+01	9.73E+00	1.11E+01
ND 221	Y	19.0	0.1	989.0	338.0	141.9	178.9	1.4	183.1	<0.01	24.055	3.84E-03	5.21E+01	1.54E+01	9.66E+00	9.65E+00
ND 222	Y	17.9	0.1	786.8	533.0	112.1	125.2	1.1	243.9	<0.01	30.14	4.99E-03	4.40E+01	1.88E+01	9.75E+00	1.37E+01
Average		19.8	0.1	963.0	400.5	134.2	159.5	1.3	216.4	<0.01	26.5	4.10E-03	4.88E+01	1.57E+01	9.78E+00	1.10E+01
Background Sites																
Average**		57.4	0.3	2,566.4	547.6	174.2	146.8	1.5	678.7	0.4	50.0	8.02E-03	9.98E+01	3.82E+01	9.27E+00	3.71E+01

**Average is of data from 17 samples, for full table see Table A2.

Produced water in the Bakken formation is highly saline with total dissolved solids ranging from 35,000 to 330,000 mg/L and are dominated by chloride, sodium, and calcium.⁵ These brines have characteristically high Br/Cl ratios (avg $4.58E^{-3}$) in addition to high concentrations of potentially toxic trace metals including Sr, B, Li, Co, Cu, Rb, Fe, Ba and Cd. (Table 4). Sodium, strontium and boron behave conservatively and thus can be plotted against chloride to observe the mixing relationships between the Bakken produced water and background waters and thus assist in categorizing surface water samples.

Type A spills in this study includes the larger Bear Den Bay spill and three other similarly impacted sites. The sites categorized as type A spills have most similar chemical composition to the Bakken produced waters indicating a mixing of the produced water with the already saline background water. Many of these sites were in intermittent flow systems or systems likely to experience flushing during heavy rain events facilitating the mixing with background waters. Similar to the produced water, type A spills have high Br/Cl ratios (avg $4.24E^{-3}$) as well as similarly low Na/Cl ratios (avg $5.94E^{-1}$). They also most closely resemble the produced water's positive Na/Cl, Mg/Cl, B/Cl, Li/Cl, SO_4/Cl , Sr/Cl, and HCO_3/TOC relationships (Figures 3, A3, and A4). A new spill site not characterized last year was ND 214, a small tributary to Antelope Creek that was potentially impacted by a spill in 2007. This site had a chloride concentration of 17,788 mg/L, a Br/Cl ratio of $3.46E^{-3}$, and a signature Na/Cl ratio of $4.77E^{-1}$ which is close to the average Na/Cl ratio $4.65E^{-1}$ observed in produced waters.

Type B spills were smaller spill events, or of an unknown volume, and somewhat isolated from flowing water with limited mixing. Type B spills had lower Br/Cl ratios (avg $2.48E^{-3}$), and higher Na/Cl ratios (avg 1.38) supporting the conclusion that they weren't mixing in the same way as Type A spills. Four new sample sites were characterized as type B spills in

this study. ND 217, ND 218, ND 224, and ND 231 all had lower Br/Cl ratios and higher Na/Cl ratios than background samples. Type B spills also had lower levels of sulfate compared to Type A spills and a lower SO_4/Cl ratio compared to background levels. They also were characteristically isolated ponds allowing for limited mixing with background water and for more intense evaporation and then the subsequent precipitation of minerals. Type B and type A spills had elevated levels of trace metals relative to background samples, including lithium, boron, and strontium. (Table 2).

Only four groundwater samples were taken for this study, and those were mostly opportunistic. ND 211 and ND 212 are shallow ground water wells located in the same impacted wetlands that ND 210 came from. ND 230 was a private drinking water well sampled after collecting soil samples at the house, and ND 235 was an artisanal spring sampled to examine the natural groundwater. Both of these samples look like background waters with low salinity and low trace metal concentrations. ND 211 and ND 212 contained elevated concentrations of produced water solutes including high chloride and sodium. The Na/Cl ratios for these samples (3.44E^{-1} and 4.86E^{-1} respectively) are closest to the average Na/Cl ratio for the Bakken produced waters of 4.65E^{-1} (Table 2). The samples also contain high sulfate that could indicate mixing with background groundwater similar to type A. However, the Br/Cl ratios for ND 211 (1.86E^{-3}) and ND 212 (1.73E^{-3}) more closely resembles the type B spill average of 2.48E^{-3} . The trace metal concentrations look much more like the type A spills with similar concentrations of lithium, boron, and barium (Table 3). Uranium was very elevated in these two samples with concentrations of $120.7\mu\text{L}$ and $157.2\mu\text{L}$ for ND 211 and ND 212 respectively. The MCL for uranium is $30\mu\text{L}$. More widespread groundwater sampling should be a focus of future studies.

Table 2: Characterization of Major Chemistry of Groundwater Samples

Sample ID	Source	Cl (mg/L)	Br (mg/L)	SO ₄ (mg/L)	HCO ₃ (mg/L)	Ca (mg/L)	Mg (mg/L)	Sr (mg/L)	Na (mg/L)	NH ₄ (mg/L)	TOC (mg/L)	Br/Cl	SO ₄ /Cl	B/Cl	Sr/Cl	Na/Cl
ND 211	Shallow Well on Site	19266.49	35.77	1045.29	422.00	3193.86	1634.82	19.72	6626.74	9.35	58.40	1.86E-03	5.43E-02	5.14E-01	9.71E-01	3.44E-01
ND 212	Shallow Well on Site	10655.38	18.40	3156.83	740.00	925.66	833.49	8.84	5183.02	<0.01	34.98	1.73E-03	2.96E-01	1.05E+00	8.05E-01	4.86E-01
ND 230	Private well	21.16	0.09	2.92	555.00	144.13	70.43	1.09	198.11	<0.01	17.07	4.10E-03	1.38E-01	6.17E+00	4.63E+01	9.36E+00
ND 235	Natural Spring	5.31	0.04	261.76	485.00	50.53	29.51	0.85	178.34	<0.01	11.17	8.22E-03	4.93E+01	5.72E+01	1.52E+02	3.36E+01

Table 3: Characterization of Trace Metals of Groundwater Samples

Sample ID	Source	Li (µg/L)	B (µg/L)	Mn (µg/L)	Co (µg/L)	Ni (µg/L)	Cu (µg/L)	Rb (µg/L)	Tl (µg/L)	Fe (µg/L)	Ba (µg/L)	Pb (µg/L)	Cd (µg/L)	U (µg/L)
ND 211	Shallow Well on Site	2531.32	9894.70	2427.51	n.d.	72.36	n.d.	77.57	1.55	0.00	968.48	1.34	7.63	120.70
ND 212	Shallow Well on Site	2020.82	11228.78	n.d.	n.d.	n.d.	n.d.	4.18	n.d.	0.00	54.87	0.76	n.d.	157.19
ND 230	Private well	58.22	130.45	n.d.	n.d.	3.63	62.71	1.77	n.d.	0.00	24.02	0.27	n.d.	26.49
ND 235	Natural Spring	64.16	303.76	119.01	0.03	n.d.	0.12	2.94	n.d.	0.00	13.30	n.d.	n.d.	n.d.

Table 4. Characterization of Trace Metals in Bakken Produced Waters, Spill Waters, and Background Waters

Sampled 2015	Li	B	Co	Ni	Cu	Rb	Fe	Ba	Cd	U	
Sample ID	Y/N	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	
Type A Spills											
ND 206	Y	2,747.0	11,885.1	n.d.	24.0	n.d.	146.6	0.0	152.3	n.d.	54.1
ND 207	Y	2,946.9	13,251.1	n.d.	29.4	n.d.	165.7	0.0	237.6	2.4	42.0
ND 208	Y	807.9	2,745.4	n.d.	15.9	6.0	8.7	0.0	102.3	n.d.	24.2
ND 226	Y	585.4	594.7	n.d.	6.5	2.3	20.4	0.0	47.3	n.d.	0.6
ND 210	Y	694.3	4,566.3	2.9	22.7	6.8	154.9	0.0	746.7	n.d.	5.8
ND 214	N	3,860.4	12,726.8	n.d.	21.5	n.d.	21.5	0.0	59.2	n.d.	101.0
Average		1,940.3	7,628.2	2.9	20.0	5.0	86.3	0.0	224.2	2.4	37.9
Type B Spills											
ND 209	Y	120.5	138.0	0.6	3.1	0.6	4.9	0.0	97.0	n.d.	1.2
ND 213	Y	124.4	89.4	0.3	2.0	n.d.	4.5	0.0	190.2	n.d.	0.3
ND 217	N	130.3	2,623.2	3.1	10.8	3.3	3.0	0.0	45.3	n.d.	5.3
ND 218	N	267.1	1,072.6	n.d.	4.7	n.d.	8.4	0.0	21.5	n.d.	2.7
ND 224	N	115.4	780.1	0.9	11.3	2.1	5.0	0.0	37.7	n.d.	10.3
ND 231	N	216.3	569.1	1.2	4.4	3.0	8.4	0.0	66.1	n.d.	3.0
Average		162.3	878.8	1.2	6.0	2.2	5.7	0.0	76.3	n.d.	3.8
Produced Water From 2015											
PW 1	-	31,476.4	225,275.4	95.1	533.1	113.9	11,746.0	19,161.6	9,210.3	21.3	0.0
PW 2	-	19,726.1	142,843.3	152.7	613.1	14.8	7,438.2	30,236.5	12,437.6	22.1	0.0
PW 3	-	2,909.8	24,995.6	2.9	9.0	13.4	342.5	686.7	26,252.1	0.5	0.0
PW 4	-	37,002.8	260,078.4	168.6	833.9	365.7	12,916.1	22,303.7	6,350.7	31.0	0.0
Average		22,778.8	163,298.2	104.8	497.2	126.9	8,110.7	18,097.1	13,562.7	18.7	0.0
Blacktail Creek											
ND 219	Y	92.9	304.6	0.3	3.3	1.0	3.0	0.0	27.2	n.d.	4.6
ND 220	Y	95.6	295.0	0.3	3.6	1.7	2.6	0.0	26.6	n.d.	4.7
ND 221	Y	92.6	292.4	0.3	3.5	1.0	2.8	0.0	24.1	n.d.	5.1
ND 222	Y	99.3	335.4	0.3	2.7	0.9	2.7	0.0	28.7	n.d.	3.2
Average		95.1	306.9	0.3	3.3	1.1	2.8	0.0	26.6	n.d.	4.4
Background Sites											
ND 201	N	27.6	54.6	0.4	10.9	12.0	2.7	0.0	33.8	n.d.	10.3
ND 202	N	182.9	301.9	2.1	20.8	7.2	7.0	0.0	39.2	n.d.	66.0
ND 203	N	31.4	127.7	0.8	4.0	n.d.	1.8	0.1	175.1	n.d.	1.1
ND 204	N	56.7	141.5	n.d.	2.0	1.3	2.5	0.0	41.8	n.d.	3.1
ND 205	N	90.6	304.2	0.9	3.3	1.3	0.8	0.2	25.5	n.d.	1.2
ND 215	N	193.4	3,876.4	1.5	10.9	4.5	3.8	0.0	36.2	n.d.	3.3
ND 216	N	116.1	743.3	n.d.	4.4	1.5	2.6	0.0	18.4	n.d.	1.0
ND 223	N	43.0	200.7	17.8	8.4	0.8	4.0	14.7	17.4	n.d.	6.5
ND 225	N	149.1	792.1	1.3	9.3	2.6	3.6	0.0	21.1	n.d.	3.2
ND 227	N	47.5	169.8	0.5	4.0	0.8	1.7	0.0	18.3	n.d.	1.0
ND 228	N	19.4	77.5	0.9	6.1	3.0	1.2	0.0	49.4	n.d.	6.7
ND 229	N	33.2	477.4	0.4	7.8	7.0	2.6	0.0	58.0	n.d.	13.8
ND 232	N	11.8	44.8	0.6	3.6	1.3	3.7	0.2	143.9	n.d.	0.8
ND 233	N	62.8	396.5	1.4	8.9	5.4	1.9	2.5	65.7	n.d.	3.7
Nd 234	N	8.7	30.7	1.0	3.8	0.4	1.7	0.1	351.2	n.d.	0.8
ND 236	N	756.1	10,091.2	2.9	16.1	7.4	3.8	0.2	21.2	0.1	8.9
ND 237	N	44.9	534.5	1.2	16.6	16.2	2.6	0.0	61.1	n.d.	11.0
Average		57.4	291.0	2.2	8.3	4.5	2.8	1.1	69.3	0.1	8.4

B. Persistent Salt and Trace Metal Contamination from Produced Water Spills:

Environmental contamination from produced water spills is thought to be persistent over many years.^{13,14} Here, we revisited six sites that showed high salt and trace metal contamination in the previous study. Originally sampled in July 2015, we sampled these sites almost a year later in June 2016 to re-examine the impacts from the produced water spills, and to characterize any change. Three of the sites revisited were type A spills, including the two largest spills in North Dakota history, the Blacktail Creek spill (11 million L), and the Bear Den Bay spill (3.8 million L). The other type A spill revisited was on the property of a private landowner, as were the other three type B spills revisited. Table 5 shows the sites side by side with major solute concentrations, TOC, and lithium, boron and strontium to observe conservative trace metal persistence.

The Bear Den site shows some of the most persistent contamination we observed. ND 206 and ND 207 are comparable to ND 102 and ND 103. ND 208 was a smaller pond off to the side that we sampled in 2016, but was not present in 2015. Between the samples there is only a slight decrease in chloride and bromide. This could be due to evaporation and dilution from rain events. Sulfate increased significantly in 2016 indicating that mixing with the high sulfate background water is continuing to happen likely through runoff after large rain events. Surprisingly ND 207 has significantly lower levels of calcium, magnesium, strontium, and sodium though ND 206 levels remain stable. This could be due to the smaller size of ND 207 allowing for increased dilution and precipitation. ND 207 also has higher levels of bicarbonate, which could indicate increased precipitation of the cations. One of the more noticeable reductions is in TOC. Organic carbon is likely being oxidized as sulfate is also increasing, potentially lowering TOC as the produced water is being mixed with the oxic background water.

The Bear Den site still displays trace metal contamination however, as lithium and boron remain elevated for both sites.

The GT site, ND 113 and ND 226, is categorized as a type A spill, mixing with background saline waters. This site shows almost identical chemical characteristics to the previous year. Only TOC significantly decreased over time, while chloride, calcium, magnesium, lithium, and boron concentrating in the 2016 sample. This is likely a result of evaporation, and indicates that concentrations will continue to increase over time without remediation.

The other three sites revisited in this study, DP1, DP2, and DP3 are type B spills. The pipeline and connector spills affecting these sites occurred in 2011 and were of a smaller volume than those affecting Bear Den and Blacktail Creek. However, these sites still displayed contamination characteristic of produced water impacts in 2015 when studied by Lauer et al. DP1, ND 128 and ND 209, was the only one of the three to show decreases in contamination. Salinity, trace metals, and TOC significantly decreased. This could have been caused by dilution as the decreases were ubiquitous; however, DP2 and DP3 showed the exact opposite. These sites showed a concentration of major ions and trace metals. The only decreases were in TOC for both sites and bicarbonate for DP2. The land where these sites are located is agricultural land, and the impact of the produced water spill is observable. Due to their ability to affect and harden soil composition and reduce osmotic pressure brines are toxic to non-salt tolerant species like the soy grown at the site.⁷ As these sites remain contaminated five years after the spill event, this raises the important issue of produced water spills and its impacts on agricultural production.

Table 5: Comparison of Revisited Site Chemistry to 2015 sites

	Cl	Br	SO ₄	HCO ₃	Ca	Mg	Sr	Na	TOC	Li	B
Sample ID	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(µg/L)	(µg/L)
Bear Den 2015											
ND102	14794.8	72.5	1713.4	279.3	1953.2	684.3	52.6	6002.8	301.0	3244.5	13139.7
ND103	16032.4	74.0	3209.7	246.8	1773.0	902.0	51.1	6754.4	265.0	3490.0	15501.0
Bear Den 2016											
ND 206	13168.9	58.1	3645.2	211.0	1644.3	930.4	50.2	6271.1	53.3	2747.0	11885.1
ND 207	14226.4	63.2	2372.2	292.0	205.3	75.4	5.9	604.2	45.9	2946.9	13251.1
ND 208	3535.5	15.6	2320.1	294.0	727.1	378.9	12.4	2408.6	54.2	807.9	2745.4
GT 2015											
ND113	996.5	5.5	4090.2	668.3	576.1	375.8	5.7	1513.3	134.0	478.3	511.2
GT 2016											
ND226	1106.3	5.0	3878.9	507.0	605.3	407.5	6.4	1431.3	31.7	585.4	594.7
DP1 2015											
ND128	269.1	0.6	945.9	465.7	187.0	148.0	0.9	298.3	160.0	212.9	193.0
DP1 2016											
ND209	94.5	0.2	579.4	371.0	154.0	98.4	0.7	129.6	49.5	120.5	138.0
DP2 2015											
ND129	5832.7	5.8	856.3	115.7	1224.9	474.7	5.9	1876.2	183.0	803.7	5358.1
DP2 2016											
ND210	6704.9	6.5	979.0	49.0	1997.9	448.1	7.6	1597.2	65.0	694.3	4566.3
DP3 2015											
ND130	188.6	0.2	387.4	345.3	108.6	90.9	0.5	99.3	94.0	79.1	38.8
DP3 2016											
ND213	329.6	0.3	469.7	443.0	159.6	135.0	0.6	170.5	51.6	124.4	89.4
Blacktail Creek 2015											
ND123	1486.8	5.2	3025.4	880.5	156.5	234.8	3.5	2028.8	207.0	476.3	3217.1
ND126	1900.3	5.9	3116.6	940.8	211.8	257.6	4.7	2282.4	220.0	542.2	3994.5
Blacktail Creek 2016											
ND219	23.0	0.1	1025.1	363.0	138.9	137.4	1.3	223.7	26.5	92.9	304.6
ND220	19.3	0.1	1051.1	368.0	143.8	138.9	1.3	214.9	25.3	95.6	295.0
ND221	19.0	0.1	989.0	338.0	141.9	134.7	1.3	183.1	24.1	92.6	292.4
ND222	17.9	0.1	786.8	533.0	112.1	102.7	1.0	243.9	30.1	99.3	335.4

C. Naturally Occurring Radioactive Matter in Bakken Brines and Spill Impacts:

Unconventional oil and gas produced waters can have high levels of naturally occurring radioactive materials (NORM), especially radium isotopes ^{228}Ra ($t_{1/2} = 5.75$ years) and ^{226}Ra ($t_{1/2} = 1600$ years).^{5, 19-21} Lauer et al. analyzed Bakken produced waters for radium activities finding total radium activities up to 64 Bq/L and an average $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio of 0.45 (Table A4). A 2014 study from the Argonne National Laboratory analyzing North Dakota scale, sludge and filter socks found similar average activity ratios of 0.6, 0.3, and 0.4 respectively.²³

Table 6: ^{228}Ra and ^{226}Ra activity in North Dakota soils/sediments

Sample ID	Origin	Description	^{228}Ra (Bq/kg)	1 σ (%)	^{226}Ra (Bq/kg)	1 σ (%)	$^{228}\text{Ra}/^{226}\text{Ra}$ (Activity Ratio)	Total Ra (Bq/kg)
Type A Spills								
NDS 204A	8/14 Tanker Spill	Closest to site	90.517	5.139	140.264	1.992	0.65	230.781
NDS 204B	8/14 Tanker Spill	Down hill from site	50.763	4.895	63.325	1.951	0.80	114.088
NDS 204C	8/14 Tanker Spill	Further downhill	36.430	5.986	43.125	2.679	0.84	79.555
NDS 204D	8/14 Tanker Spill	Site background	37.882	5.697	38.383	2.896	0.99	76.265
NDS 207	7/14 Bear Den Spill	Sediment from ND 207	35.515	7.025	49.935	2.796	0.71	85.451
NDS 253	7/14 Bear Den Spill	Close to Site Origin	48.00	6.66	68.13	2.61	0.70	116.132
NDS 252A	Tanker Spill	Site Background	32.19	7.20	26.61	4.06	1.21	58.797
NDS 252B	Tanker Spill	Site Origin	62.59	5.27	71.46	2.29	0.88	134.051
NDS 252C	Tanker Spill	Site Origin	59.82	5.89	59.43	2.99	1.01	119.253
NDS 214	Impacted Stream Sediment	Antelope Creek Spill Site	49.986	7.025	70.282	2.796	0.71	120.268
Average			60.281	5.812	78.815	2.440	0.791	139.096
Type B Spills								
NDS 223	GT Spill	Recent Spill Soil	45.157	5.341	49.632	2.615	0.91	94.790
NDS 251A	5/15 pipeline spill	Down hill 0.2 miles	29.38	7.96	31.96	3.82	0.92	61.340
NDS 251B	5/15 pipeline spill	Adjacent to Site	29.44	7.82	29.04	3.70	1.01	58.482
NDS 263	Unknown	Impacted soil	34.98	8.32	51.06	3.11	0.69	86.038
Average			34.74	7.36	40.42	3.31	0.88	75.16
Blacktail Creek								
NDS 119	1/15 Blacktail Spill	Spill Site	25.780	6.064	31.444	2.628	0.82	57.224
NDS 221	1/15 Blacktail Spill	Upstream	8.302	7.151	8.357	3.945	0.99	16.659
Average			17.041	6.607	19.900	3.287	0.907	36.942
Background								
NDS 211			25.084	7.462	22.467	4.612	1.12	47.551
NDS 212			25.736	6.010	24.833	3.352	1.04	50.569
NDS 257			21.71	5.55	21.71	3.18	1.00	43.417
NDS 260			27.67	7.49	29.08	3.68	0.95	56.748
NDS 262			15.89	10.20	14.06	5.15	1.13	29.954
Average			23.22	7.34	22.43	4.00	1.05	45.65

When Radium is spilled into the environment it can be retained in the soils by adsorbing to solids, or through incorporation into radium rich minerals such as barite (BaSO_4).¹⁹ Radium can concentrate in soils and sediments through these processes and persist after the brine has been removed. Using USGS PHREEQC modelling software, Lauer et al. found that North Dakota background waters contain high amounts of aragonite, barite, calcite, and dolomite suggesting that incorporation could be a possible mechanism for radium adsorption. To corroborate this theory total radium activity was far lower in the spill water, but was elevated in soils.⁵ Radium adsorption efficiency is dependent on the water to sediment ratio, water salinity, water concentrations of bivalent cations like calcium, soil type and composition, organic matter content, clay mineral cation exchange capacity, oxide content, porosity, and soil/sediment particle size.¹⁹⁻²¹ Highly saline solutions like Bakken produced water could inhibit radium adsorption to soils making contamination more widespread and potentially concentrating the radium in downstream soils. However, soils with high levels of calcium, magnesium and sulfate contribute to the removal of radium from solution by providing sorption sites, or by contributing ions that increase precipitation and co-precipitation reactions.¹⁹ Bakken soils high in sulfate and magnesium could thus facilitate the precipitation and therefore accumulation of radium. Bakken region background waters are known to be high in magnesium and sulfate and any mixing could also result in increased adsorption and accumulation.

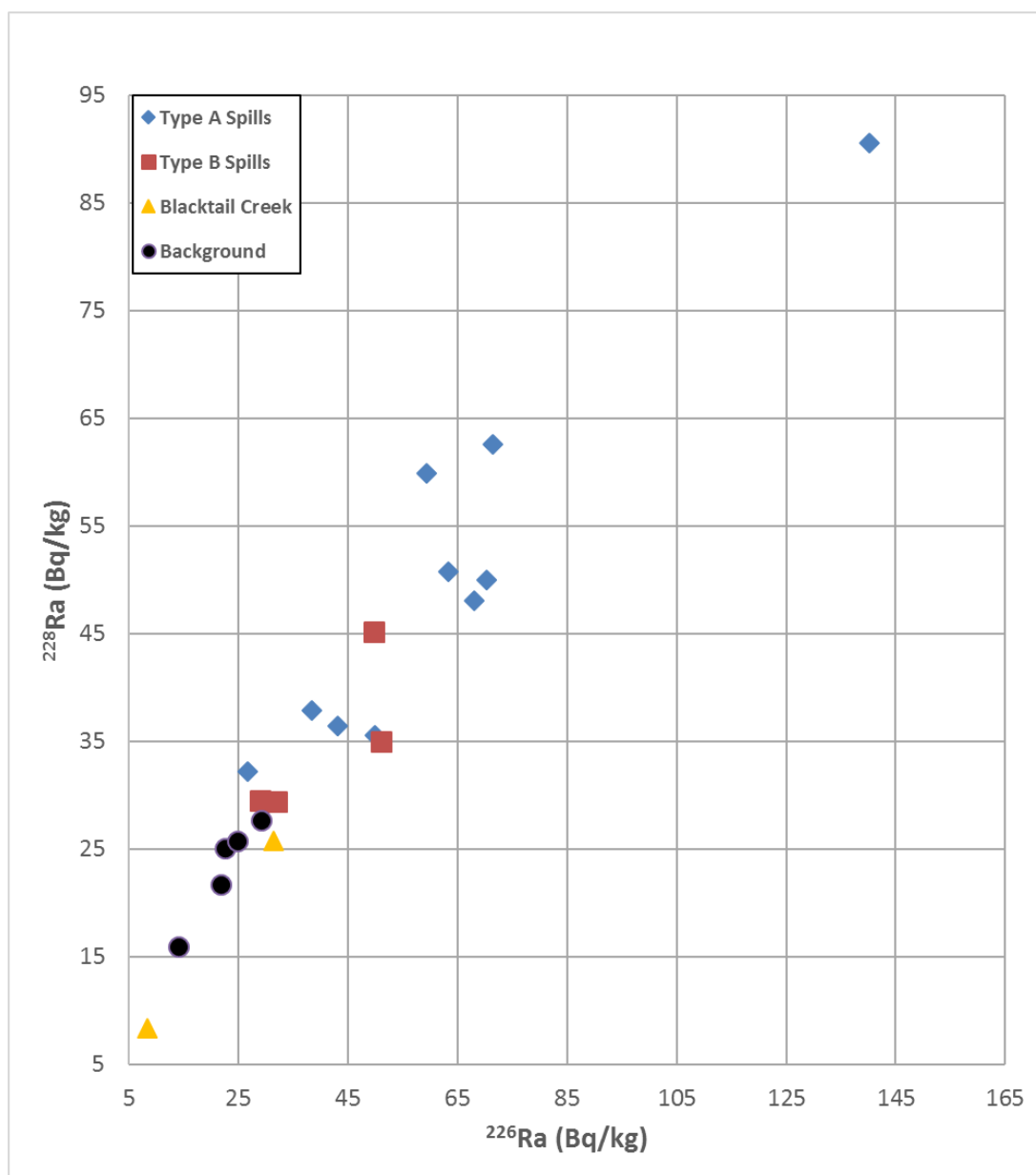


Figure 4. This graph displays the correlation between radium isotopes ^{226}Ra and ^{228}Ra in soils and sediments for spill types A and B, background sites, and Blacktail Creek. Note that type A and B spills have higher amount of ^{226}Ra compared to ^{228}Ra indicating potential impact from produced waters. Of particular interest is the Blacktail Creek samples which are comparable to background levels, with the spill site sample well within background and the upstream sample the lowest point on the graph.

Here we found elevated radium activity in soils and sediments impacted by produced water spills (Table 6). The impact of produced water is reflected by lower $^{228}\text{Ra}/^{226}\text{Ra}$ activity

and higher total radium (Figure 4).⁵ After removing the background samples for the type A spill sites, the average $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio was 0.791 with an average total radium of 139.096 Bq/kg. The type B spills had a higher average $^{228}\text{Ra}/^{226}\text{Ra}$ activity of 0.88 and an average total radium of 75.16 Bq/kg, which was still lower than the background average $^{228}\text{Ra}/^{226}\text{Ra}$ activity of 1.05 and higher than the background average total radium 45.65 Bq/kg.

On the site of a August 2014 tanker spill we collected sediment samples but no water was present. NDS 204A-D showed decreasing $^{228}\text{Ra}/^{226}\text{Ra}$ activity as distance from the spill increased (0.65-0.99). The sample closest to the spill site had the highest total radium we observed 230.781 Bq/kg. This runs counter to the thought that increased salinity decreases sorption at the site. However, as the spill was much smaller than Bear Den where that relationship was observed in 2015 it could have been a factor of slower flow, or a lower water to sediment ratio.

Judging radium persistence at sites is difficult with grab sediment and soil samples due to difficulty in selecting the exact same spot sampled previously. In 2015 Bear Den sites ranged from 107-212 Bq/kg, whereas here our samples were 85.45 and 116.13. The GT site also showed similar disparity with 142 total radium in 2015 and 94.79 in 2016. The DP sites showed consistent total radium levels with DP1 in 2015 ranging from 31-53 and in 2016 43.42. The DP2 site was measured at 33-49 total radium in 2015 and 46.55 in 2016. The DP3 site was similar with a 2015 total radium range of 46-52 and 50.57 in 2016. However, these concentrations are not significantly higher than background levels. It should be noted that ^{228}Ra has a half-life of 5.75 years and our sediment samples were measured up to a little over a seven months after they were collected. Ratios and total radium in our sediment samples may be lower than those

determined by Lauer et al. (2016) because our activity ratios have not been corrected for ^{228}Ra decay between when our sediment samples were collected and when they were analyzed.

D. Successful Remediation of Blacktail Creek: The Blacktail Creek spill was the largest reported produced water spill in North Dakota history. Reported January 6, 2015 an underground produced water pipeline crossing underneath Blacktail Creek had leaked an estimated 74,000 barrels (11 million liters) of highly saline brine contaminating the creek.²⁴ The pipeline was operated by Summit Midstream Partners, LLC., a Texas based company that focuses on developing, owning and operating midstream energy infrastructure assets that are strategically located in the core producing areas of unconventional resource basins, primarily shale formations, in the continental United States. The company immediately shut off the pipeline, but not before the damage was done. Lauer et al. 2016 characterized the spill in June 2015⁵ and a USGS study by Cozzarelli et al.¹⁴ also assessed the effects of the momentous produced water spill.

Lauer et al. collected a water sample at the spill site, two downstream samples, and two upstream samples (Table 3 shows the Site and closest downstream sample). The study also collected six sediment/soil samples to better characterize the spill site (Table A3). The survey of the water chemistry showed high salinity indicative of produced water contamination with chloride concentrations above 1400 mg/L, bromide above 5 mg/L, greater than 2000 mg/L sodium, and high concentrations of ammonium. The site also had elevated levels of trace metals including lithium, boron, manganese, strontium, and barium. Most alarming were the levels of radium activity in the sediments at the spill site, with total radium of 553 Bq/kg, 1606 Bq/kg and 4684 Bq/kg compared to upstream sediments (45 Bq/kg). These were the highest radium levels

obtained in the 2016 study indicating heavy impact and likely persistent accumulation in the soils and sediments surrounding the site.

The recent USGS study published in 2016 focused solely on the Blacktail Creek spill site. In February 2015 and in June 2015 they collected water and sediment samples at the spill site, 4.7 km downstream, 7.2 km downstream where it joins the Little Muddy River, 22.9 km downstream on the Little Muddy River, and 43.8 km downstream with upstream reference sites for both Blacktail Creek and the Little Muddy River.¹⁴ The study analyzed water samples for major ions, trace metals, semi-volatile hydrocarbons, light (C₁-C₆) hydrocarbons, and sediment samples for barium, strontium, and radium activities. Similar to Lauer et al. 2016 they found elevated amounts of salinity both at the site and downstream. Chloride concentrations were found at a maximum 1030 mg/L at the site 4.7km downstream in February with much lower concentrations observed in June. Bromide, sulfate, and sodium were also found at concentrations several orders of magnitudes higher than background downstream of the spill site. Elevated amounts of trace metals including manganese, barium, and strontium were observed downstream with manganese reaching a maximum value of 470 µ/L, well above the MCL of 50 µ/L. Sediments analyzed for radium found a peak total radium of 754 Bq/kg with activity ratios ranging from 0.62 downstream to 0.90 at the spill site. The study did find significant estrogenic inhibition at the 4.7km and 7.2 km downstream sites though the effect diminished greatly by June and were back to reference levels measured in the Little Muddy River. Their study concluded that the initial remediation effectively removed some types of contamination, but allowed others to persist. However, the site continued to be remediated and the last report in the incident summary was on March 16, 2017 and detailed ongoing geoprobing and well monitoring for chloride concentrations.²⁴

The remediation of Blacktail Creek has been an arduous process. As of February 14, 2017 the total amount of liquid pumped and disposed of was 1,552,380 barrels (>185 million liters), 149.49 tons of solid waste were removed, and 16.53 tons of municipal waste were disposed.²⁴ The remediation process began the day after the report on January 7 with absorbent booms placed along the length on Blacktail Creek up to the confluence with the Little Muddy River approximately 7.3 km downstream and vacuum extraction of the contaminated water for disposal at a deep well injection site. Pumping from the creek continued almost around the clock and low flow conditions were observed as early as January 8. Multiple underflow dams were constructed to excavate the oil that was released with the brine and to help control flow of the creek with limited success as warmer conditions melted the ice in the creek causing an increase in flow.²⁵ Ice was also being removed at this time and disposed of with excavated contaminated soil. Rope skimmers and snare boom pumps were employed January 26 to assist in oil recovery as the underflow dams were being overtopped. Stantec also dug Intercept trenches completed on January 31 with more planned to prevent contaminated groundwater from reaching the creek, water flowing into the trenches exceeded 7000 mg/L of chloride. Additional trenches were dug and vacuum pumping continued both from the trenches, and at sections of the creek with elevated chloride levels above 1000 mg/L. Monitoring wells were completed by February 10 and a routine sampling schedule was implemented to identify target areas. By February 13, 2015 liners were installed in the containment areas and erosion control was implemented in vulnerable areas to prevent the release of sediment to the creek. By March an estimated 6000 barrels (715,442 Liters) were being removed daily. An 800 foot sheet pile containment wall was completed April 9th, to further prevent infiltration of groundwater into the creek. Soils were divided into cells the more heavily impacted areas of the creek bank were excavated and

washed; excavated soils were dewatered before being removed to a disposal site along with the water used for washing. Clean soils were installed on excavated areas and reseeded for grass and the project was considered completed and the final report submitted April 27, 2015. A map of the implemented control measures can be found in the Appendix (Figure A5).

Though arduous, the remediation measures taken were very effective at reducing the contamination observed at Blacktail Creek in 2015. When we sampled the spill site in June 2016 almost all contaminants of concern were reduced to background levels or below (Figure 3, Tables 1-4, Figure 4). All major solutes including chloride, bromide, sulfate, calcium, magnesium, and sodium were significantly reduced. Trace metal concentrations of strontium, lithium and boron were also reduced to background levels. Most impressive was the recovery of the sediment radium levels from a total radium range of 553 Bq/kg to 4684Bq/kg in 2015 with an average activity ratio of 0.68 to 57.2 Bq/kg and 16.7 Bq/kg total radium in 2016 with activity ratios of 0.82 and 0.99 respectively. Figure 4 shows the relationship between ^{226}Ra and ^{228}Ra and the Blacktail Creek samples are some of the lowest and are observably within background. Though the remediation costs were undisclosed confidential business information, the strategy seemed to have worked on Blacktail Creek.

IV. Implications and Conclusions: Produced waters resulting from unconventional oil development in the Bakken region contain extremely high levels of salts, predominantly chloride, sodium, calcium and bromide.^{5,13-18} These brines also contain elevated concentrations of trace metals barium, manganese, strontium, boron, and lithium. Sites identified as impacted by produced water spills based on the dominant water chemistry and ionic ratios contained salt and trace metal concentrations that dwarfed background levels by a magnitude or greater. Chloride, sodium, manganese, and uranium surpassed ND Class II Surface Water MCLs,

Livestock MCLs, and drinking water MCLs respectively at spill sites.²⁶⁻²⁸ Aside from being of ecological concern, Bear Den Bay occurred upstream of the drinking water intake in Lake Sakakawea and could've potentially posed a human health risk had it been closer. Several studies have shown endocrine disrupting effects in rodent, fish, and in vitro related to exposure to produced waters.^{14,29,30} The ecological risk from the highly saline spills is more clear and observable as salinity devastates plant life.⁷

Comparing Bakken produced water chemical ratios including Br/Cl, Na/Cl, Sr/Cl, and B/Cl to sampling sites enabled categorization of sites into type A spills experiencing mixing with background waters, type B spills that are more isolated and can concentrate contaminants through evaporation, and background sites (Figure 3). $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios were also characteristic of the different spill types with type A site ratios closer to those seen in produced water than type B which were still lower significantly lower than background (Table 4, Figure 4).

This study followed up on the 2016 study by Lauer et al. to re-characterize spills a year later and examine whether contamination from produced waters persists in the environment. Of the six sites examined in both studies, solute and trace metal concentrations persisted in all but two, with one of those sites being Blacktail Creek a location that experienced extensive remediation (Table 3). The other site DP1 likely experienced natural dilution as it was a much smaller spill initially.

Blacktail Creek, the site of the largest spill in North Dakota history, was one of the most contaminated sites characterized by Lauer et al. 2016, especially in terms of radium sediment contamination.⁵ This study re-examined the site and observed solute and trace metal contamination reduced to background levels. Total radium activity in the sediment similarly

deceased by magnitudes in the year between the two studies. This was only made possible through exhaustive site remediation including the systematic removal of 1,552,380 barrels (>185 million liters) of contaminated water, 149.49 tons of solid waste, and 16.53 tons of municipal waste. This was the only site studied remediated in such a fashion, explaining why the other sites still show signs of persistent contamination.

From 2007 to 2015, brine spills were reported in North Dakota with 3x the frequency compared to oil spills over the same time frame.¹⁴ As the occurrence of produced water spills increases directly in relationship to unconventional oil development we will likely see more spills of a large scale in increasing frequency. Left un-remediated like the Bear Den Bay spill, contamination will persist in the environment harming ecological health, and potentially affecting human health if spills occur near drinking water sources. Future research should seek to characterize new spill sites including more widespread groundwater sampling near areas of high production and well pad density, develop methods to examine produced water organic constituents after their release into the environment and evaluate their endocrine disruption capabilities and persistence, evaluate the costs of brine spill site remediation so the industry is more educated on the financial risks associated with large spills, and conduct in situ Human Health and Ecological risk assessments of produced water spills in the environment. This study confirmed and expanded the knowledge of how produced water spills can be identified in the environment using conservative relationship chemistry and showed how persistent the contamination is without extensive remediation as seen at the Blacktail Creek site.

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Appendix:

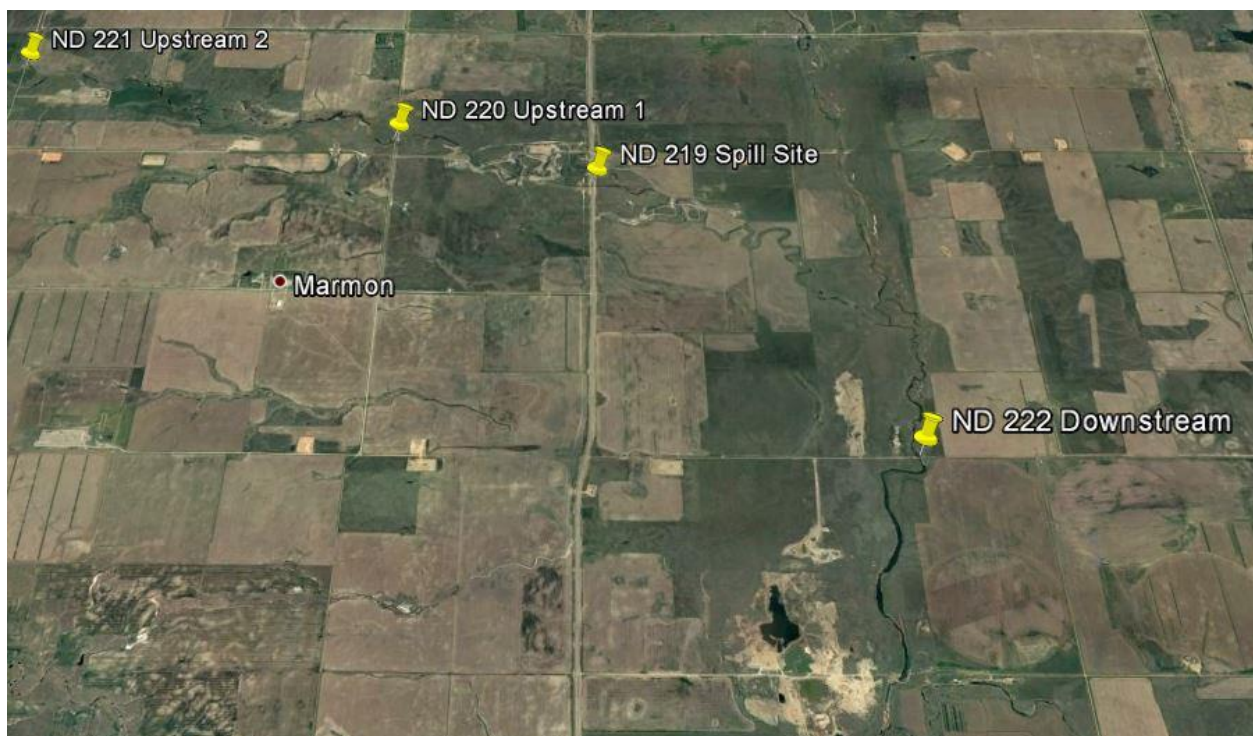


Figure A1: Locations of sampling sites on Blacktail Creek.



Figure A2: Location of Bear Den Bay sampling site in relation to the spill. Note two things: the observable red-orange tint of the spill water pooled in the bay, and the spill path that has been flushed and reseeded with grass.

Sample ID	Lat (N)	Long (W)	Spill Date (If known)	Spill Volume (bbls)	Reported Spill Cause	Sampled Water Type	Description
Type A Spills							
ND 206	47.782817	-102.650983	7/7/2014	24,000	Pipeline	Small pond, standing water	Bear Den Bay spill, largest pond, most uphill
ND 207	47.783050	-102.651650	7/7/2014	24,000	Pipeline	Small pond, standing water	Bear Den Bay Spill, smaller pond downhill of ND206
ND 208	47.782917	-102.651550	7/7/2014	24,000	Pipeline	Small pond, standing water	Bear Den Bay Spill, smaller pond next to ND207
ND 226	47.868983	-102.950217	Spring 2016			Wetlands/pond	Downstream of recent spill
ND 210	48.797883	-101.343667	7/20/2011	~300	Pipeline	Large pond in Field	Ponding of spill waters in low lying field
ND 214	48.010650	-102.779350	~2007			Small Stream	Runoff stream tributary to Antelope Creek
Type B Spills							
ND 209	48.777183	-101.312333	2/25/2011	~300	Connection Leak	Wetlands/pond	0.1 miles from disposal site
ND 213	48.808917	-101.200833				Wetlands/pond	0.1 miles from disposal site
ND 217	48.016367	-102.784333				Small pond	adjacent to pipeline connector
ND 218	47.834950	-102.848483				Wetlands/pond	Ponding of possible spill waters in low lying field
ND 224	47.868250	-102.946800				Small stream/pond	Upstream of ND 226
ND 231	47.32603	-102.8495				Small pond, standing water	Adjacent to well pad
Blacktail Creek							
ND 219	48.398267	-103.624433	1/17/2015	70,000	Pipeline	Large stream	Blacktail creek spill site
ND 220	48.403283	-103.646267	1/17/2015	70,000	Pipeline	Large stream	Blacktail creek 1.1 miles upstream
ND 221	48.411733	-103.689583	1/17/2015	70,000	Pipeline	Large stream	Blacktail creek 3.11 miles upstream
ND 222	48.372883	-103.594133	1/17/2015	70,000	Pipeline	Large stream	Blacktail creek 2.51 miles downstream
Groundwater							
ND 211	48.798333	-101.343550				Shallow well	Adjacent to ND 210 pond
ND 212	48.809000	-101.20035				Shallow well	Adjacent to ND 210 pond
ND 230	47.44181667	-102.812267				Private well	Home owner outside of Killdeer, ND
ND 235	47.84465	-102.452933				Natural spring	Artisanal Spring on private land
Background							
ND 201	47.606800	-102.847617				Standing water/runoff stream	Sourced from runoff, no nearby development
ND 202	47.605517	-102.849833				Standing water/runoff stream	Downstream of ND 201
ND 203	47.749600	-102.383933				Small pond	Pond thought to be impacted by spill from tanker flipping
ND 204	47.749600	-102.390733				Lake Sakakawea	Large lake and water source for Fort Berthold Reservation
ND 205	47.633850	-102.677083				Wetlands	Wetlands 0.2 miles from well pad
ND 215	48.014183	-102.778483				Antelope Creek/Large stream	Stream containing Halophytes
ND 216	48.012600	-102.776150				Antelope Creek/Large stream	Downstream of ND 215
ND 223	47.86771667	-102.867717				Wetlands/pond	0.1 miles from well pad
ND 225	47.882467	-102.952450				Wetlands/pond	Nearby well pad
ND 227	47.865933	-102.948883				Wetlands/pond	Background wetlands
ND 228	47.08678333	-103.44445				Stock pond for cattle	Potentially impacted by nearby oil spill
ND 229	47.06321667	-103.442117				Franks Creek/Large stream	Potentially impacted by nearby oil spill
ND 232	47.32933333	-102.885717				Stock pond for cattle	Dwonhill from 2008 spill
ND 233	47.36073333	-102.886917				Spring Creek/Large stream	High tanker traffic area
ND 234	47.84573333	-102.466317				Small stream	Nearby well pad
ND 236	47.8323	-102.487167				Stock pond for cattle	Background pond
ND 237	47.97083333	-102.711233				Small pond	Nearby natural gas pipeline spill

Table A1: Additional information about sampling site locations, known spill dates and volumes, spill cause (if reported, water type, and descriptions of the site.

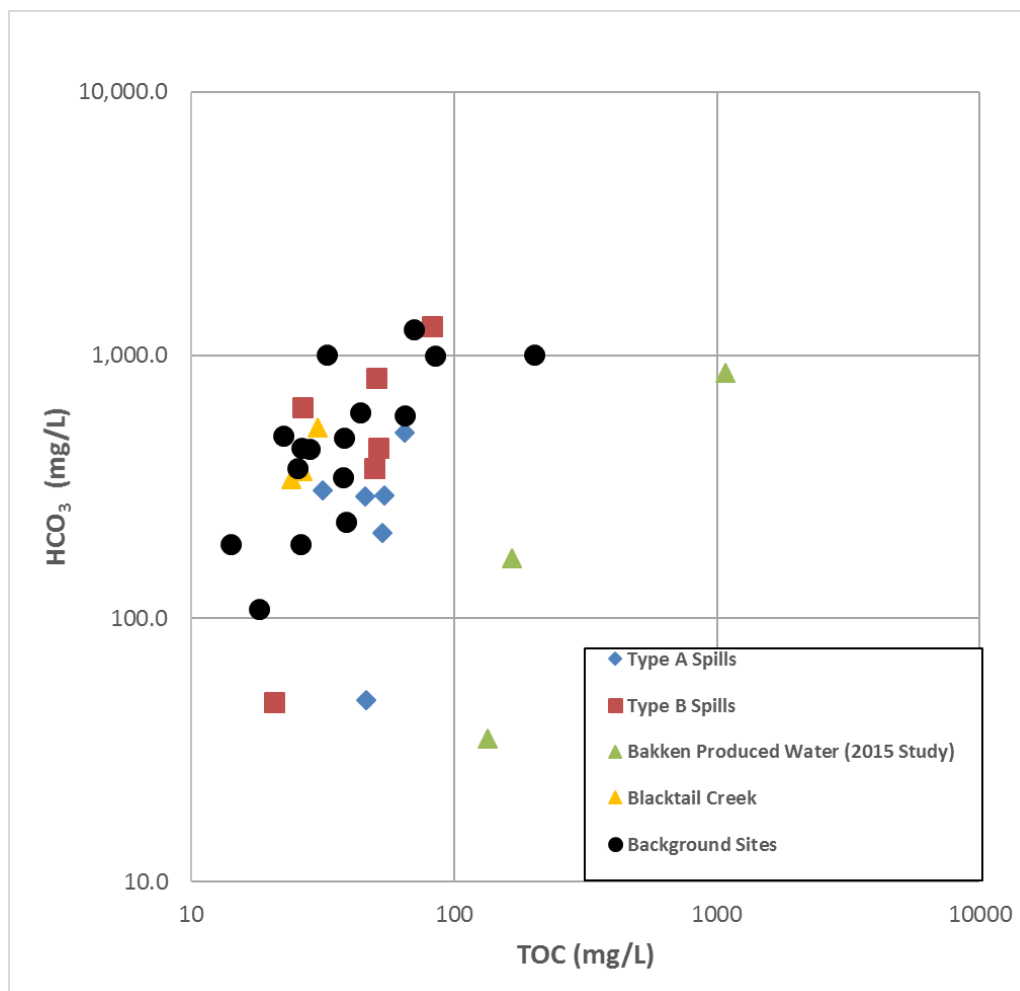


Figure A3: Graph showing the correlation between HCO_3^- and TOC concentrations. Note that the background sites are positively correlated, and that the produced waters sampled in 2015 are also correlated, but have higher TOC concentrations due to left over oil residues.

Table A2: Characterization of Major Chemistry of Bakken Produced Waters, Spill Impacted Waters, and Background Waters

Sample ID	Sampled 2015 Y/N	Cl (mg/L)	Br (mg/L)	SO ₄ (mg/L)	HCO ₃ (mg/L)	Ca (mg/L)	Mg (mg/L)	Sr (mg/L)	Na (mg/L)	NH ₄ (mg/L)	TOC (mg/L)	B/Cl	SO ₄ /Cl	B/Cl	Sr/Cl	Na/Cl
Type A Spills																
ND 206	Y	13,168.9	58.1	3,645.2	211.0	1,644.3	930.4	47.4	6,271.1	0.4	53.3	4.41E-03	2.77E-01	9.03E-01	2.88E+01	4.76E-01
ND 207	Y	14,226.4	63.2	2,372.2	292.0	205.3	726.0	55.9	604.2	1.4	45.855	4.44E-03	1.67E-01	9.31E-01	2.77E+02	4.25E-02
ND 208	Y	3,535.5	15.6	2,320.1	294.0	727.1	378.9	11.3	2,408.6	<0.01	54.2	4.42E-03	6.56E-01	7.77E-01	1.55E+01	6.81E-01
ND 226	Y	1,106.3	5.0	3,878.9	507.0	605.3	425.6	6.0	1,431.3	<0.01	65	4.49E-03	3.51E+00	5.38E-01	9.92E+00	1.29E+00
ND 210	Y	6,704.9	6.5	979.0	49.0	1,997.9	448.1	7.4	1,597.2	10.1	46.505	9.76E-04	1.46E-01	6.81E-01	3.71E+00	2.38E-01
ND 214	N	17,788.0	61.6	4,514.4	307.0	1,694.9	1,270.3	54.6	8,490.4	<0.01	31.695	3.46E-03	2.54E-01	7.15E-01	3.22E+01	4.77E-01
Average		9,965.0	40.7	3,346.2	322.2	975.4	746.2	35.0	3,841.1	0.9	49.4	4.24E-03	9.72E-01	7.73E-01	7.18E+01	5.94E-01
Type B Spills																
ND 209	Y	94.5	0.2	579.4	371.0	154.0	98.4	0.6	129.6	0.1	49.545	1.68E-03	6.13E+00	1.46E+00	4.20E+00	1.37E+00
ND 213	Y	329.6	0.3	469.7	443.0	159.6	135.0	0.6	170.5	<0.01	51.55	1.00E-03	1.42E+00	2.71E-01	3.86E+00	5.17E-01
ND 217	N	537.6	1.5	2,343.3	1,290.0	148.0	115.8	2.5	1,660.9	<0.01	82.7	2.74E-03	4.36E+00	4.88E+00	1.84E+01	2.62E+00
ND 218	N	770.6	2.4	4,540.2	820.0	212.2	243.0	4.8	2,332.3	<0.01	50.45	3.05E-03	5.89E+00	1.39E+00	2.46E+01	2.59E+00
ND 224	N	586.2	2.8	1,843.0	635.0	466.3	313.9	2.8	432.9	<0.01	26.57	4.80E-03	3.14E+00	1.33E+00	5.93E+00	7.39E-01
ND 231	N	481.5	1.5	2,334.7	48.0	328.0	182.9	3.8	765.5	<0.01	20.63	3.11E-03	4.85E+00	1.18E+00	1.17E+01	1.59E+00
Average		1,357.8	2.2	1,869.9	522.3	495.1	219.6	3.2	1,012.7	5.1	46.9	2.48E-03	3.71E+00	1.60E+00	1.03E+01	1.38E+00
Produced Water From 2015																
PW 1	-	119,989.0	558.0	128.0	35.0	12,033.0	1,001.0	774.0	47,217.0	2,110.0	134.3	4.65E-03	1.07E-03	1.88E+00	6.45E-03	3.94E-01
PW 2	-	75,892.0	384.0	102.0	169.0	8,573.0	741.0	551.0	34,745.0	1,200.0	166.3	5.06E-03	1.34E-03	1.88E+00	7.26E-03	4.58E-01
PW 3	-	21,728.0	91.6	0.0	856.0	372.0	118.0	33.1	12,271.0	44.8	1,080	4.22E-03	0.00E+00	1.15E+00	1.52E-03	5.65E-01
PW 4	-	136,220.0	601.0	293.0	15,346.0	1,299.0	970.0	60,571.0	2,520.0	2,520.0	144.9	4.41E-03	2.15E-03	1.91E+00	7.12E-03	4.45E-01
Average		88,457.3	408.7	130.8	353.3	9,081.0	789.8	582.0	38,701.0	1,468.7	381.4	4.58E-03	1.14E-03	1.70E+00	5.59E-03	4.65E-01
Blacktail Creek																
ND 219	Y	23.0	0.1	1,025.1	363.0	138.9	162.2	1.4	223.7	<0.01	26.465	3.28E-03	4.45E+01	1.32E+01	9.97E+00	9.72E+00
ND 220	Y	19.3	0.1	1,051.1	368.0	143.8	171.7	1.4	214.9	<0.01	25.29	4.30E-03	5.44E+01	1.53E+01	9.73E+00	1.11E+01
ND 221	Y	19.0	0.1	989.0	338.0	141.9	178.9	1.4	183.1	<0.01	24.055	3.84E-03	5.21E+01	1.54E+01	9.66E+00	9.65E+00
ND 222	Y	786.8	533.0	786.8	533.0	112.1	125.2	1.1	243.9	<0.01	30.14	4.99E-03	4.40E+01	1.88E+01	9.75E+00	1.37E+01
Average		19.8	0.1	963.0	400.5	134.2	159.5	1.3	216.4	<0.01	26.5	4.10E-03	4.88E+01	1.57E+01	9.78E+00	1.10E+01
Background Sites																
ND 201	N	26.9	1.2	10,526.4	233.0	67.2	25.8	0.8	465.8	<0.01	38.88	4.34E-02	3.91E+02	2.03E+00	1.17E+01	1.53E+01
ND 202	N	11.9	0.0	7,008.0	606.0	412.2	300.3	0.0	2,612.8	0.0	43.79	8.37E-04	5.87E+02	2.53E+01	1.34E+01	1.81E+02
ND 203	N	7.3	0.0	194.4	496.0	133.7	53.7	0.8	47.6	0.2	22.47	5.48E-03	2.65E+01	1.74E+01	5.62E+00	6.48E+00
ND 204	N	10.9	0.0	221.3	191.0	59.8	25.6	0.6	72.8	<0.01	14.11	2.96E-03	2.02E+01	1.29E+01	9.68E+00	6.65E+00
ND 205	N	2.2	0.0	247.6	1,001.0	17.8	25.9	0.1	442.3	<0.01	32.825	4.50E-03	1.11E+02	1.37E+02	8.37E+00	1.62E+02
ND 215	N	476.2	1.2	3,065.1	992.0	135.5	123.3	2.7	1,872.9	<0.01	84.9	2.55E-03	6.44E+00	8.14E+00	2.03E+01	3.27E+00
ND 216	N	91.7	0.3	1,843.7	345.0	132.0	142.9	1.7	631.4	<0.01	37.63	2.91E-03	2.01E+01	8.10E+00	1.32E+01	6.88E+00
ND 223	N	131.5	0.8	2,093.4	439.0	699.1	222.9	2.1	255.0	1.2	28.095	6.25E-03	1.59E+01	1.53E+00	2.96E+00	1.94E+00
ND 225	N	37.6	0.2	4,442.6		384.1	361.7	4.6	1,386.5	<0.01	74.95	5.83E-03	1.18E+02	2.11E+01	1.19E+01	3.69E+01
ND 227	N	31.9	0.1	118.5	109.0	79.1	45.0	0.4	105.1	<0.01	18.03	2.70E-03	3.71E+00	5.32E+00	4.89E+00	3.30E+00
ND 228	N	41.3	0.1	794.5	485.0	31.5	51.3	0.3	464.6	<0.01	38.26	1.60E-03	1.93E+01	1.88E+00	1.04E+01	1.06E+01
ND 229	N	22.2	0.1	988.5	374.0	80.8	39.0	0.7	481.3	<0.01	25.365	2.65E-03	4.45E+01	2.15E+01	7.99E+00	1.83E+01
ND 232	N	7.3	0.0	14.9	191.0	31.1	11.0	0.1	17.9	<0.01	26.135	2.58E-03	2.04E+00	6.12E+00	4.44E+00	1.32E+02
ND 233	N	3.1	0.0	134.9	1,258.0	15.9	12.3	0.1	482.0	0.2	70.3	5.89E-03	4.33E+01	1.27E+02	6.84E+00	1.32E+02
ND 234	N	1.6	0.0	18.6	443.0	104.5	30.0	0.1	5.3	<0.01	26.22	3.00E-02	1.20E+01	1.98E+01	1.38E+00	3.42E+00
ND 236	N	47.2	0.5	10,707.5	1,007.0	517.8	984.4	10.5	1,529.8	<0.01	202.5	1.07E-02	2.27E+02	2.14E+02	1.68E+01	1.61E+01
ND 237	N	25.4	0.1	1,209.6	591.0	59.5	41.1	0.4	665.4	<0.01	64.8	5.49E-03	4.75E+01	2.10E+01	7.68E+00	2.40E+01
Average**		57.4	0.3	2,566.4	547.6	174.2	146.8	1.5	678.7	0.4	50.0	8.02E-03	9.98E+01	3.82E+01	9.27E+00	3.71E+01

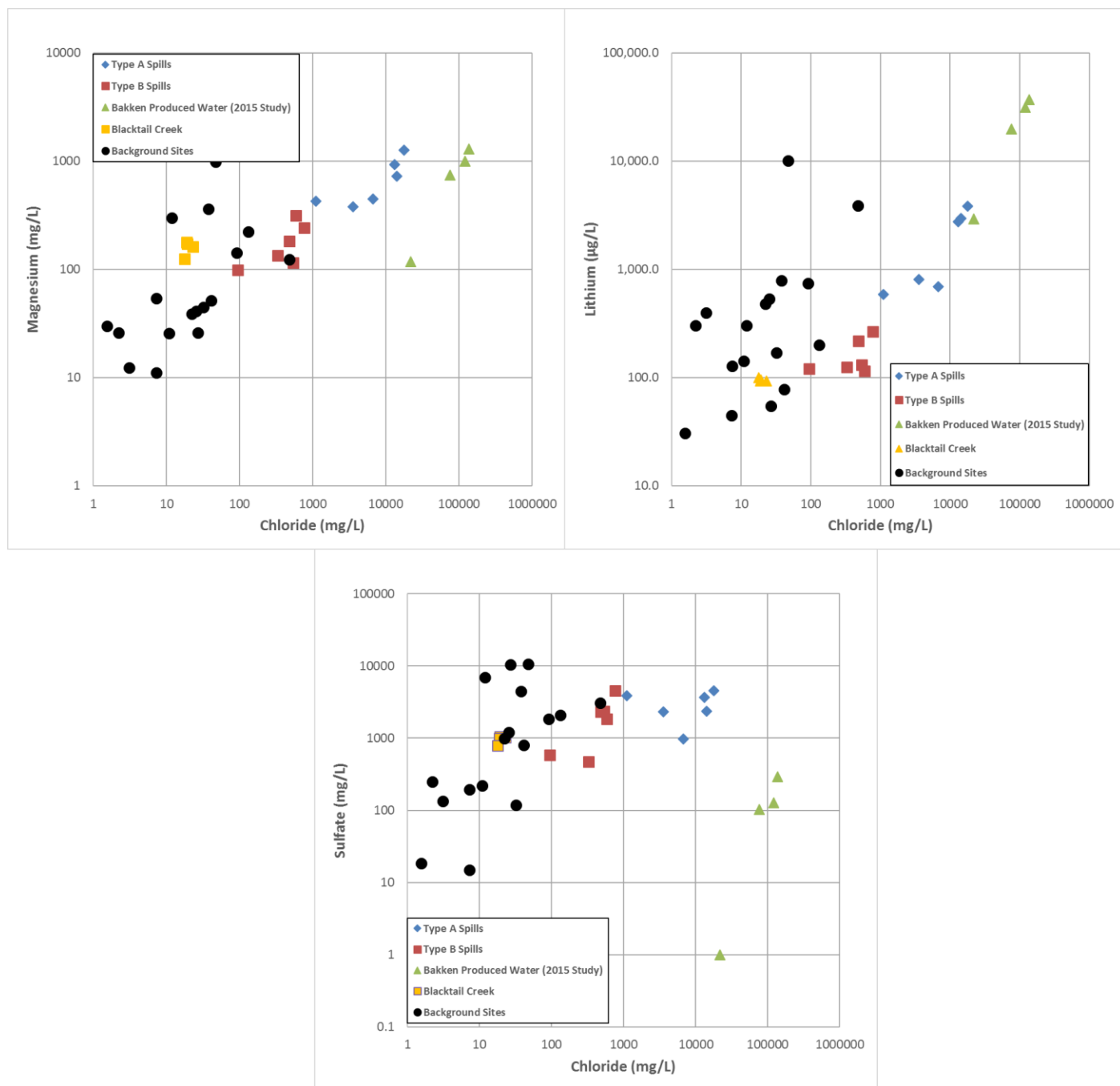


Figure A4: Graphs showing the correlations of Mg to Cl, Li to CL, and SO₄ to Cl for Type A and B Spills, Bakken Produced Water, Blacktail Creek, and Background sites. Note that the Produced Water stands out in the SO₄ to Chloride relationship, as it is much lower in sulfate and higher in chloride compared to the natural surface waters. The Type A Spills also have a similar relationship, though not as distinct after mixing with the background water. Also, note that the Blacktail Creek samples are again well within background levels.

Table A3: ^{228}Ra and ^{226}Ra in 2015 North Dakota soils/sediments from Lauer et al. 2016

Sample Name	^{228}Ra (Bq/kg)	1 σ (%)	^{226}Ra (Bq/kg)	1 σ (%)	$^{228}\text{Ra}/^{226}\text{Ra}$ (Activity ratio)	Total Ra (Bq/kg)
Type A Spills						
ND102A	48	4.4	59	1.8	0.82	107
ND102B	52	3.5	70	1.3	0.73	122
ND102C	49	3.3	72	1.3	0.68	121
ND102D	82	3.3	129	1.1	0.64	212
ND102E	53	3.6	65	1.6	0.82	118
ND103	87	2.8	103	1.1	0.84	190
ND113	76	3.4	66	1.8	1.15	141
ND123	1883	1.5	2802	0.4	0.67	4684
ND123A	227	1.8	326	0.7	0.69	553
ND123B	647	1.2	959	0.3	0.67	1606
Type B Spills						
ND128A	19	4.2	12	2.7	1.60	31
ND128B	16	9.2	21	4.1	0.75	37
ND128C	19	4.5	18	2.1	1.03	37
ND128E	28	7.1	25	3.8	1.12	53
ND128D	18	3.0	18	1.4	1.00	35
ND129	26	5.6	24	2.8	1.09	49
ND129A	23	4.4	22	2.2	1.06	45
ND129B	19	5.7	20	2.7	0.97	38
ND129C	16	5.3	17	2.2	0.91	33
ND130A	23	4.6	23	2.2	1.02	46
ND130B	25	3.7	26	2.1	0.96	52
ND131	28	4.6	31	2.3	0.90	59
Background Sites						
ND106	29	5.4	32	2.4	0.89	61
ND111	34	3.2	41	1.4	0.81	75
ND112	37	3.4	32	1.8	1.15	70
ND117	13	4.7	30	1.6	0.43	43
ND125	23	5.0	22	2.5	1.06	45
ND101	23	2.5	27	1.2	0.88	50
ND108	26	4.0	27	1.8	0.96	53
ND109	30	6.5	29	3.0	1.03	60
ND118	28	4.4	32	2.1	0.88	60
ND122	22	2.2	25	0.8	0.86	47
ND124	9	10	12	3.7	0.75	21
ND114	23	4.8	24	2.1	0.98	47
ND116	27	4.7	24	2.3	1.15	51
ND107	26	3.9	66	1.3	0.39	91
ND110	35	3.8	64	1.3	0.54	98

Table A4: ^{228}Ra and ^{226}Ra in Bakken Produced Waters from Lauer et al. 2016

Sample Name	^{228}Ra (Bq/L)	1 σ (%)	^{226}Ra (Bq/L)	1 σ (%)	$^{228}\text{Ra}/^{226}\text{Ra}$ (Activity ratio)	Total Ra (Bq/L)
PW1	13.0	7.4	30.2	2.5	0.43	43.2
PW2	18.9	11	44.8	3.7	0.42	63.7
PW3	no data	---	no data	---	---	---
PW4	9.6	6.4	19.5	2.4	0.49	29.1

