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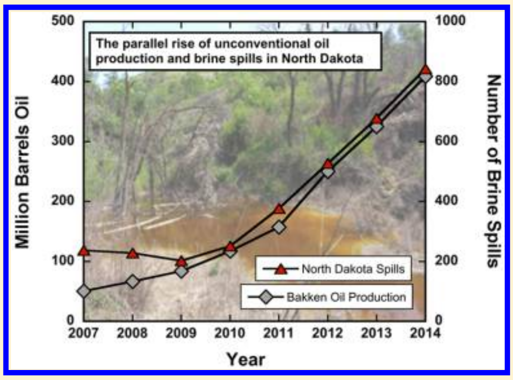
Brine Spills Associated with Unconventional Oil Development in North Dakota

Nancy E. Lauer, Jennifer S. Harkness, and Avner Vengosh*

[†]Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States

Supporting Information



ABSTRACT: The rapid rise of unconventional oil production during the past decade in the Bakken region of North Dakota raises concerns related to water contamination associated with the accidental release of oil and gas wastewater to the environment. Here, we characterize the major and trace element chemistry and isotopic ratios ($^{87}Sr/^{86}Sr$, $\delta^{18}O$, $\delta^{2}H$) of surface waters ($n = 29$) in areas impacted by oil and gas wastewater spills in the Bakken region of North Dakota. We establish geochemical and isotopic tracers that can identify Bakken brine spills in the environment. In addition to elevated concentrations of dissolved salts (Na, Cl, Br), spill waters also consisted of elevated concentrations of other contaminants (Se, V, Pb, NH_4) compared to background waters, and soil and sediment in spill sites had elevated total radium activities (^{228}Ra + ^{226}Ra) relative to background, indicating accumulation of Ra in impacted soil and sediment. We observed that inorganic contamination associated with brine spills in North Dakota is remarkably persistent, with elevated levels of contaminants observed in spills sites up to 4 years following the spill events.

INTRODUCTION

With the discovery of new oil fields and advances in drilling technology, notably hydraulic fracturing and horizontal drilling, unconventional oil and gas production from the Bakken region in North Dakota has been rising significantly since 2007. In 2014, the Bakken region was producing an average of over 1 million barrels of oil per day, compared to production levels that consistently lingered at approximately 100 thousand barrels per day before 2007.[1] This rapid rise in production has been made possible by intense development of oil and gas infrastructure in western North Dakota, including approximately 9700 unconventional wells that have produced an estimated 31.4 × 10^9 gallons (118.9 × 10^9 L) of oil and gas wastewater (OGW).[2]

OGW includes highly saline produced and flowback waters that, in the Bakken region, can exceed 300 g/L of total dissolved solids (TDS).[3,4] In addition to high salinity, OGW often contains a number of toxic trace elements and naturally occurring radioactive materials (NORM) in elevated concentrations that can be threatening to local water quality if released to the environment.[5−11] Previous studies have shown contamination of local surface water resources from unconventional oil and gas development due to the release of OGW to the environment in the form of (1) effluents to local streams and rivers following inadequate treatment by water treatment facilities,[5−7,9] (2) dust suppressants and deicing agents,[11] and (3) leaks and spills.[8,12] The release of OGW to the environment has been linked to salt, trace metal, and NORM contamination of local surface water, shallow groundwater, and stream sediments.[8,13−15]

In North Dakota, the high occurrence of OGW spills is potentially threatening the quality of surface and drinking water resources. Since the beginning of the rise of unconventional oil extraction and hydraulic fracturing in 2007, there have been approximately 3900 brine spills reported to the North Dakota Department of Health by well operators (Figure 1); brine spills are defined as the accidental release of brine that may potentially impact groundwater or surface water.[16] In North Dakota, OGW is primarily transported by pipes or trucks and stored in enclosed containers onsite prior to disposal via deep well injection. Reported spills often occur during transport to injection sites via pipelines or during filling or emptying of storage tanks. Unlike other areas in the U.S. where decades of conventional oil and gas exploration have generated a legacy of contamination, the exploration rates of conventional oil and gas in North Dakota were significantly lower than recent unconventional operations. Therefore, recent OGW spills are directly associated with recent unconventional oil extraction. Previous research on the impact of hydraulic fracturing in the Bakken region has been limited to two studies showing groundwater contamination from one site[17] and temporal changes in surface water and shallow groundwater quality from

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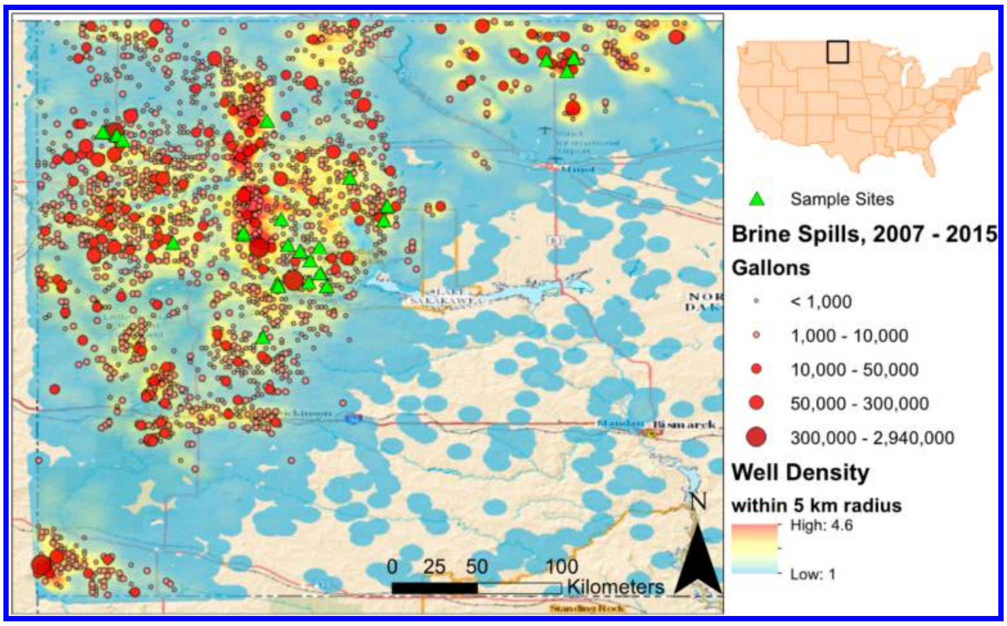

Figure 1. Map of western North Dakota that includes well density (number of wells per 5 km radius), reported brine spills from 2007 to 2015 (red circles), and sampling sites of samples collected in July 2015 (green triangles). Note the association between spill locations and well density, with higher occurrences of spills in areas of high well density. Spill data were compiled from the North Dakota Department of Health and include both contained and uncontained brine spills.[16] Oil well data were downloaded from the North Dakota Industrial Commission, Oil and Gas Division.[37]

three sites.[18] Both studies found evidence of OGW contamination in surface water and groundwater, highlighting the need for a comprehensive understanding of the dynamics of brine spill water chemistry and the potential for long-term impacts.

Here, we evaluate the impact of OGW spills on the inorganic water quality of surface water and NORM levels in soil from spill sites in North Dakota. The study is based on chemical and isotopic analyses of (1) the Bakken produced water ($n = 4$), (2) surface waters impacted by recent brine spills ($n = 10$) associated with unconventional energy development in the Bakken region of North Dakota, and (3) background surface water in western North Dakota ($n = 19$). Previous studies have shown that surface water in North Dakota is typically saline with elevated levels of sodium and sulfate relative to other areas in the U.S.[18−20] The highly mineralized background water could mask the identification of brine spills. Consequently, in this study we used multiple geochemical tracers to characterize the OGW spills and identify their occurrence in the environment. We hypothesize that the chemistry of the Bakken brines is sufficiently different from the local background saline surface water and that geochemical tracers such as Br/Cl and $^{87}Sr/^{86}Sr$ could be used to detect the OGW source in spill sites. The objectives of this study are to (1) characterize the geochemistry of spill water associated with unconventional oil production in the Bakken region, (2) establish geochemical tools to identify spill water in the environment, and (3) assess the environmental implications of brine spills and the fate of spill-water contaminants in impacted areas.

■ MATERIALS AND METHODS

Sample Collection. Twenty-nine surface water samples and 37 grab sediment and soil samples were collected in western North Dakota (Figure 1) in July 2015, as well as 4 produced water samples from the Bakken formation of the Williston Basin. In the sampling campaign, we collected water samples from surface waters impacted by reported spill events as well as samples from surface waters possibly impacted by the release of brine due to proximity of these waters to well pads or disposal sites with the aim of identifying contamination. Reported spills sampled include the two largest spill events in North Dakota's history, the Bear Den Bay Spill (referred to as samples ND102 and ND103) and the Blacktail Creek Spill (ND123 and ND126). In the Bear Den Bay Spill, an underground pipeline leak in July 2014 caused approximately 24000 barrels (3.8 million L) of brine to flow down a ravine and into the Bear Den Bay, approximately a quarter mile (0.4 km) upstream of the drinking water intake in Lake Sakakawea. The Blacktail Creek Spill, also resulting from a pipeline leak, occurred in January 2015 and released nearly 70000 barrels (11 million L) of brine near Blacktail Creek, which flows into the Little Muddy River, a tributary of the Missouri River. We also collected water samples from surface waters impacted by smaller spills. These include a 300 barrel (48,000 L) brine spill that occurred in February 2011 (ND128) and another 300 barrel brine spill that occurred in July 2011 (ND129), both in Bottineau County in northern North Dakota. Additional information on sample collection protocols, sample site locations, and sample descriptions is provided in the Supporting Information (Figures S1 and S2; Table S1).

Data Analyses. Major anions were measured by ion chromatography (IC) using a Thermo Fisher Dionex IC, major cations were measured by direct current plasma optical emission spectrometry (DCP-OES), and trace elements were measured by VG PlasmaQuad-3 inductively coupled plasma mass spectrometry (ICP-MS). Alkalinity was measured by titrating the sample with HCl to pH 4.5. Total organic carbon (TOC) measurements were conducted on a Shimadzu TOC-V CPH total carbon analyzer with a TNM-1 nitrogen module (Shimadzu Scientific Instruments). Stable oxygen and hydrogen isotopes ($\delta^{18}O$ and δ^2H) were measured at the Duke Environmental Isotope Laboratory (DEVIL) by continuous flow isotope ratio mass spectrometry using a ThermoFinnigan

Table 1. Major Chemistry and Isotopic Ratios of Bakken Produced Waters, Spill Waters, and Background Waters

sample	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)	$^{87}Sr/^{86}Sr$	$\delta^{18}O$	δ^2H
Type A Spills												
ND102	14795	72.5	1713	279	1953	684	52.6	6003	9.14	0.70973	−10.6	−82.5
ND103	16032	74.0	3210	247	1773	902	51.1	6754	42.4	0.70960	−5.9	−73.8
ND113	996	5.5	4090	668	576	376	5.67	1513	0.62	0.70787	−14.3	−109.0
ND123	1487	5.2	3025	880	156	235	3.48	2029	21.0	0.70968	−7.5	−90.5
ND126	1900	5.9	3117	941	212	258	4.70	2282	17.0	0.70971	−8.9	−97.8
avg	**7042**	**32.6**	**3031**	**603**	**934**	**491**	**23.5**	**3716**	**18.0**	**0.70932**	**−9.5**	**−90.7**
Type B Spills												
ND120	207	0.22	464	306	111	101	0.46	102	0.76	0.70980	−6.3	−66.6
ND128	269	0.56	946	466	187	148	0.89	298	0.40	0.70999	−3.3	−74.9
ND129	5833	5.8	856	116	1225	475	5.94	1876	<0.01	0.70923	−2.4	−54.8
ND130	189	0.17	387	345	109	91	0.49	99.3	0.19	0.71029	−6.7	−67.9
ND131	18703	20.5	2739	110	1381	2220	8.53	6829	0.32	0.71011	−6.8	−71.9
avg	**5040**	**5.5**	**1078**	**268**	**603**	**607**	**3.26**	**1841**	**0.42**	**0.70989**	**−5.1**	**−67.2**
Produced Water												
PW1	119989	558	128	35.0	12033	1001	774	47217	2110	0.71044		
PW2	75892	384	102	169	8573	741	551	34745	1200	0.71046		
PW3	21728	91.6	0.0	856	372	118	33.1	12271	44.8	0.70939		
PW4	136220	601	293		15346	1299	970	60571	2520	0.71044		
avg	**88457**	**409**	**131**	**353**	**9081**	**790**	**582**	**38701**	**1469**	**0.71018**		
Background Sites												
avg[a]	**21.0**	**0.73**	**1658**	**687**	**121**	**104**	**1.41**	**733**	**0.93**	**0.70820**	**−10.5**	**−101**

[a] Reflects the average of data from 19 samples.

TCEA and Delta + XL mass spectrometer. Strontium isotopes ($^{87}Sr/^{86}Sr$) were measured by thermal ionization mass spectrometry (TIMS) using a Thermo Fisher Triton. The average $^{87}Sr/^{86}Sr$ of NIST SRM-987 was $0.710264 \pm 5.8 \times 10^{-6}$ (1σ) over the course of this study.

Radium isotopes (^{226}Ra and ^{228}Ra) were measured in spill waters, produced waters, and grab soil and sediment samples at the Duke University Laboratory for Environmental Analysis of Radionuclides (LEARN) using a Canberra broad energy germanium gamma detector calibrated with a standard reference ore (DL-1a). Ra was extracted from spill waters (2−25 L) and concentrated on ∼10 g of MnO fiber.[21] Prior to γ analysis, fibers, filtered brines, and oven-dried soils and sediments were packed in 40 mL snap lid Petri style dishes that were then wrapped with electrical tape and coated with wax to prevent the escape of gaseous ^{222}Rn ($t_{1/2}$ = 3.8 days). Samples then incubated for at least 21 days in order for ^{226}Ra to reach radioactive secular equilibrium with its short-lived daughter ^{214}Pb ($t_{1/2}$ = 27 min). ^{226}Ra was analyzed through the ^{214}Pb (351 kEv) peak and ^{228}Ra was analyzed through the ^{228}Ac (911 kEv) peak. Samples were counted for 12−24 h to minimize statistical counting error, which was typically less than 5% (1σ).

■ RESULTS AND DISCUSSION

Chemical Characterization of Water Sources. Evaluation of the chemical data reveals background water and two types of spill water (defined as type A and type B spills) in the study area. Background water is highly saline (mineralized) water (TDS up to 5000 mg/L) with Na-SO_4−HCO_3 composition, high pH (up to 9.3), high TOC (300 mg/L), low Cl (typically <35 mg/L), high Br/Cl (∼3×10^{-2} molar ratio), and relatively low $^{87}Sr/^{86}Sr$ ∼0.70824 ± 0.0006 (n = 19) (Table 1). The high salinity observed in background waters in the study area cannot be explained by halite dissolution, given the low Cl concentrations and high Br/Cl ratios. Additionally, the chemical composition of the saline surface water is different from the composition of the Bakken brines, ruling out the possibility of naturally occurring brine seeps. HCO_3 is highly correlated to TOC concentrations (Figure S3), suggesting that the majority of the DIC in the highly mineralized background water is derived from oxidation of organic matter. This is consistent with low $\delta^{13}C$-DIC values (mean = -11 ± 2.9‰) that reflect oxidation of C4 type plants that are typical in arid environments (Table S4). Saline waters with elevated sulfate were previously reported for surface waters and wetlands in North Dakota,[18−20] and Sr isotope ratios measured in background waters in this study are consistent with Sr isotope ratios previously reported for uncontaminated North Dakota groundwaters.[17]

USGS data[22] and new data generated in this study (Tables 1 and 2) indicate that produced water from the Bakken formation is highly saline (TDS of 35000−330000 mg/L) and characterized by a typical Na−Ca−Cl composition. The Bakken brines have high Br/Cl (∼2×10^{-3} molar ratio; Figure 2, Table 1) and high $^{87}Sr/^{86}Sr$ (0.71018 ± 0.0005; Figure 3). Although the number of produced water samples analyzed in this study is relatively limited (n = 4), our data are consistent with previously unpublished Bakken produced water data from the USGS (n = 12; mean $^{87}Sr/^{86}Sr$ = 0.71039; Br/Cl ∼ 2×10^{-3}; mean $\delta^{18}O$ = +3‰ and mean δ^2H = −44‰)[22] as well as isotope data reported by Rostron and Holmden (mean $^{87}Sr/^{86}Sr$ = 0.70956; mean $\delta^{18}O$ = +5‰ and mean δ^2H = −40‰).[23] In addition to the elevated concentrations of major elements (Na, Cl, Br), our data show that the Bakken brines are enriched in metals, metalloids, and other potential contaminants (Se, V, Sr, B, Mn, Ni, Cd, Cu, Zn, Ba, Pb, Ra, NH_4) that have human and ecological health implications (Figure 2, Table 2).

Table 2. Trace Metals in Bakken Produced Waters, Spill Waters, and Background Waters

sample ID	Li (μg/L)	B (μg/L)	Al (μg/L)	V (μg/L)	Mn (μg/L)	Co (μg/L)	Ni (μg/L)	Cu (μg/L)	Zn (μg/L)	Se (μg/L)	Rb (μg/L)	Tl (μg/L)	Fe (μg/L)	Ba (μg/L)	Pb (μg/L)	Cd (μg/L)
Type A Spills																
ND102	3244	13140	202	148	3418	8.8	44	21	88	95	211	5.9	2673	392	8.3	2.5
ND103	3490	15501	137	171	839	4.9	25	25	52	132	236	4.7	2468	274	8.0	3.4
ND113	478	511	28	12	1924	0.7	4.3	4.4	10	8.4	22	0.0	771	54	0.5	0.0
ND123	476	3217	26	22	598	0.7	0.7	2.6	12	6.8	56	0.1	211	62	0.8	0.0
ND126	542	3995	41	25	811	0.7	0.0	2.8	25	7.2	71	0.0	79	70	1.0	0.5
avge	**1646**	**7273**	**87**	**76**	**1518**	**3.2**	**15**	**11**	**38**	**50**	**119**	**2.2**	**1240**	**171**	**3.7**	**1.3**
Type B Spills																
ND120	67	224	12	4.9	107	0.6	2.7	2.3	15	1.1	4.0	0.0	161	110	0.2	0.0
ND128	213	193	9	10	1555	1.5	5.2	1.5	4.0	1.2	7.9	0.0	271	78	0.3	0.1
ND129	804	5358	17	73	1984	2.4	14	4.9	12	49	44	0.1	1517	512	2.6	0.0
ND130	79	39	9	4.7	306	0.4	0.8	0.5	3.4	1.4	3.2	0.0	148	117	0.0	0.0
ND131	1196	1155	86	218	725	2.9	28	28	24	172	5.3	0.3	1901	194	6.0	1.4
avg	**472**	**1394**	**27**	**62**	**935**	**1.5**	**10**	**7.5**	**12**	**45**	**13**	**0.1**	**800**	**202**	**1.8**	**0.3**
Produced Water																
PW1	31476	225275	196	962	16672	95	533	114	12512	859	11746	198	19162	9210	558	21
PW2	19726	142843	861	602	13129	153	613	15	3786	630	7438	124	30236	12438	144	22
PW3	2910	24996	292	148	216	2.9	9.0	13	19	141	342	1.7	687	26252	4.8	0.5
PW4	37003	260078	1100	1020	15839	169	834	366	17122	969	12916	213	22304	6351	3481	31
avg	**22779**	**163298**	**612**	**683**	**11464**	**105**	**497**	**127**	**8360**	**650**	**8111**	**134**	**18097**	**13563**	**1047**	**19**
Background Sites																
avg[a]	**103**	**502**	**87**	**3.6**	**304**	**0.9**	**4.3**	**3.6**	**6.8**	**1.1**	**3.5**	**0.0**	**335**	**52**	**0.2**	**0.1**

[a] Reflects the average of data from 19 samples.

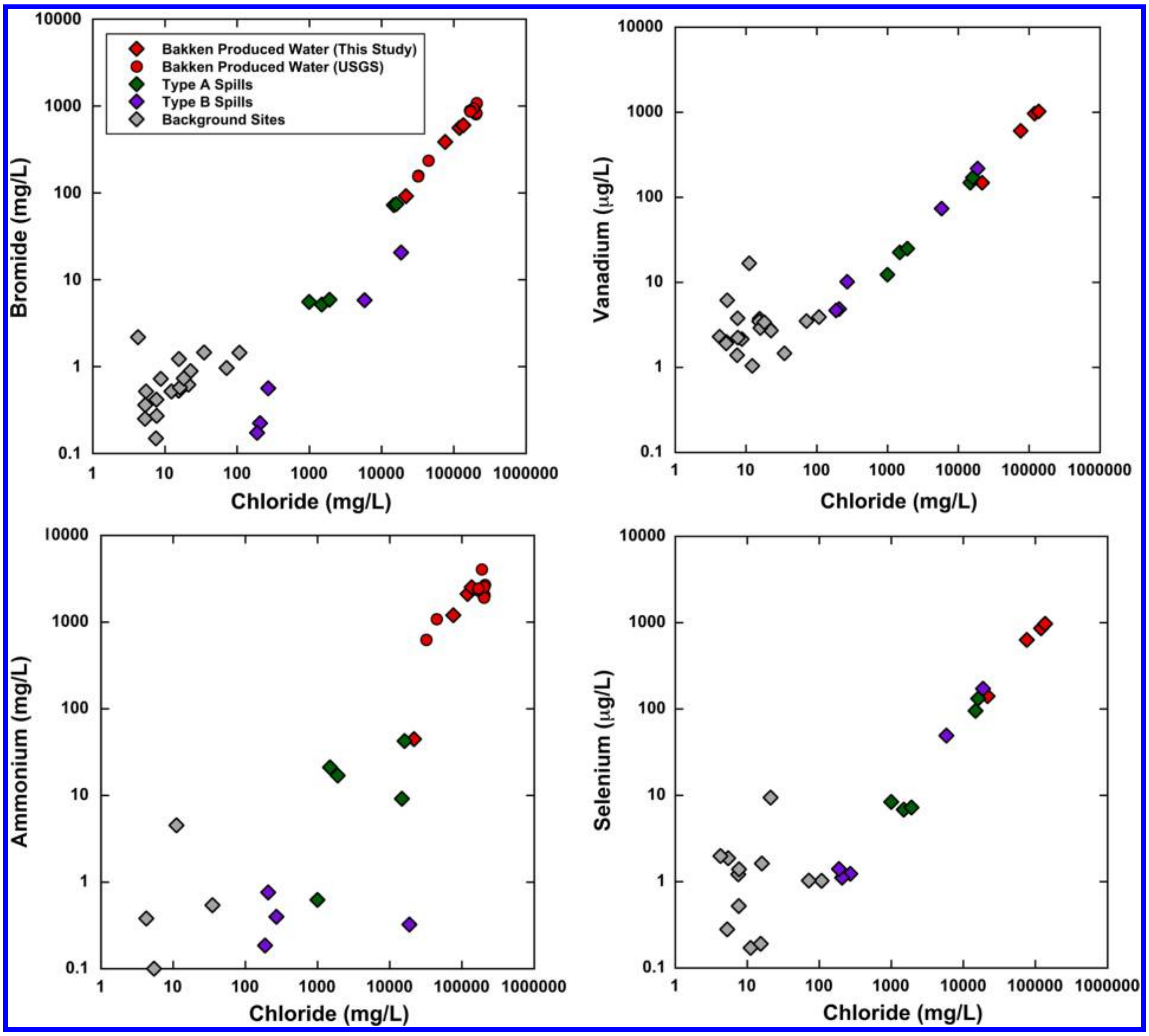

Figure 2. Bromide, selenium, vanadium, and ammonium versus chloride concentrations (log scale) in Bakken produced waters, spill waters, and background waters. Spill waters were defined on the basis of their chemical composition and resemblance to the Bakken brines (type A spills) relative to chemical fractionation induced from recycling of the Bakken brines (type B spills). Note that type A spills show linear correlations between bromide, vanadium, and selenium to chloride, indicating a conservative mixing relationship between the Bakken brines and background water.

The type A spills include the large spills at Bear Den Bay and Blacktail Creek. Type A spill water has a chemical composition that reflects the mixing of the Bakken brines with the saline background water and has relatively high Br/Cl (1.9×10^{-3} molar ratio; Figure 2) and relatively high B/Cl, Sr/Cl, and Li/Cl ratios (Figure S4). In type A spills, the magnitude of contamination depends on the relative mixing proportions of the brine and local surface water. Type B spills were generally much smaller and isolated from other water sources, which would likely promote more intense evaporation and the subsequent precipitation of minerals. Based on the distinctively low Br/Cl (5.5×10^{-4} molar ratio) of the type B spills, we propose that they originated from evaporation of the brines, followed by secondary mineral precipitation, and redissolution. As a result, type B spill water has a chemical composition that is different from simple mixing of the Bakken brines with background saline water.

We simulated the evaporation of type A spill water and evaluated the saturation index (SI) of minerals using PHREEQC software.[24] The SI is defined as SI = log(IAP/K_{sp}), where IAP is the ionic activity product and K_{sp} is the apparent equilibrium solubility product. Our simulation shows that calcite and barite minerals are supersaturated for the Type A spill waters (samples ND102 and ND103), and 5-fold and 30-fold evaporation would generate solutions that are supersaturated for gypsum and halite, respectively. We therefore suggest that extensive evaporation of spill water would result in supersaturation and secondary mineral precipitation. Redissolution of these minerals would generate Na−Cl saline water with relatively low Br/Cl ratios compared to the Bakken brines that is consistent with the chemistry of type B spill water.

Identification of Spill Water in the Environment. Surface waters defined as background waters in this study are relatively saline, which is consistent with previous studies of North Dakota surface waters.[18−20] As a result, high salinity alone cannot necessarily reveal the presence of OGW in the environment. Additionally, we identified two types of spill water, one that mimics the Bakken brines (type A) and another

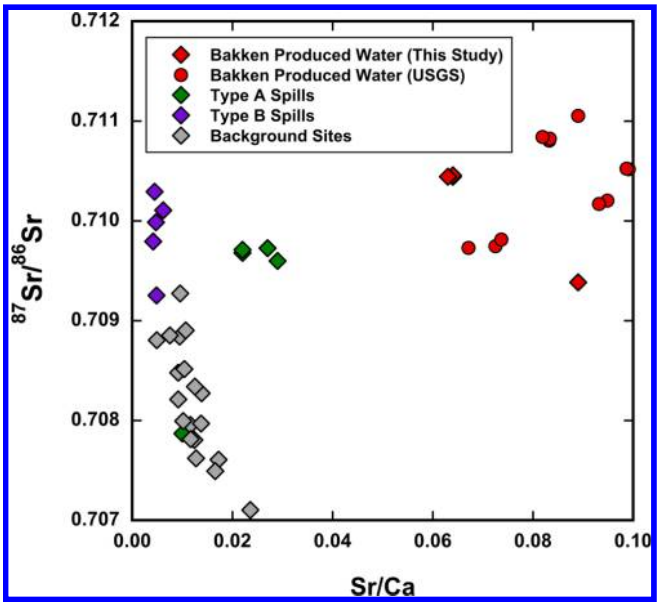

Figure 3. ^{87}Sr/^{86}Sr vs Sr/Ca (mass) ratios in Bakken produced waters, spill waters, and background waters. Note the large Sr isotopic and Sr/Ca ratio differences between the Bakken brines and background surface water in the study area. The ^{87}Sr/^{86}Sr ratio of the highly mineralized background water decreases with Sr/Ca, indicating a Sr source with a conspicuously lower ^{87}Sr/^{86}Sr signature as opposed to the relatively high ^{87}Sr/^{86}Sr ratios of the Bakken brines and spill waters. This distinction verifies that both type A and type B spill waters originated from the Bakken oil and gas wastewater.

(type B) that has a different chemical composition. Consequently, we posit that accurate identification of OGW in the environment in North Dakota requires several independent geochemical tracers.

While the chemical composition of type A spill water reflects the composition of Bakken brines diluted with local surface water, type B water had relatively lower Br/Cl ratios. Mean Br/Cl in type A spill water was not statistically different from the Bakken brines, while mean Br/Cl in type B spill water was statistically lower than both the Bakken brines and Type A waters ($p < 0.01$). Type A spill water also contained several elements (Li, B, Sr) that were positively correlated with Cl, and their ratios to Cl (Li/Cl, B/Cl, Sr/Cl) in the spill waters were similar to the ratios measured in the Bakken brines (Figure S4). We suggest that these elements behave conservatively like Cl, and thus, their concentrations in the spill water reflect the mixing relationships between the Bakken brines and background water.

The Sr isotope composition of type A spill water (^{87}Sr/^{86}Sr = 0.70932 ± 0.0008) is similar to that of type B (^{87}Sr/^{86}Sr = 0.70989 ± 0.0004). The differences in mean ^{87}Sr/^{86}Sr among type A spill, type B spill, and the Bakken produced water samples are not statistically significant, while differences in mean ^{87}Sr/^{86}Sr in type A spill, type B spill, and Bakken produced water compared to background surface water are highly statistically significant ($p < 0.01$). This confirms the salt recycling model and that type B spills originated initially from the Bakken OGW. Consequently, the use of Sr isotopes as an independent tracer for the origin of the spills is important because Sr isotope ratios are not affected by precipitation and dissolution of secondary minerals, while ionic ratios like Br/Cl could be affected by salt dissolution and differ from the expected Bakken brine composition.

The δ^{2}H−δ^{18}O slope of 5.4 ($r = 0.92$) in background waters was similar to the δ^{2}H−δ^{18}O slope of the spill waters (Figure S5). The mixing of the background water with the Bakken brines (δ^{18}O > +5‰, δ^{2}H > −40‰)[23] would therefore result in a similar slope resulting from naturally occurring evaporation of surface waters. Furthermore, the relative mixing relationship based on the chloride mass-balance suggests that type A spills contain ∼10% brine, which would not change the overall stable isotope composition of the spill water. We conclude that the stable water isotopes cannot be used as sole indicators for brine contamination in highly evaporative areas in North Dakota. The δ^{18}O and δ^{2}H of type B spills are relatively higher than those of type A, although the salinity of type B water is lower. This apparent discrepancy reflects the different origins of the two spill types; type A spills originated from mixing of the Bakken brines with background waters with lower salinity and lower δ^{18}O and δ^{2}H, while type B likely originated from recycling of salts from evaporation, salt precipitation, and dissolution that resulted in further enrichment of ^{18}O and ^{2}H in the residual saline water. We conclude that Sr isotopes are the most effective tracer of OGW in the environment in North Dakota, as they are not impacted by evaporation and cycles of salt precipitation and dissolution.

NORM in the Bakken Brines and Impact on Spill Sites. Produced waters can have elevated levels of naturally occurring radioactive materials (NORM), primarily the long-lived radium isotopes ^{228}Ra ($t_{1/2}$ = 5.75 years) and ^{226}Ra ($t_{1/2}$ = 1600 years).[10,25−28] Bakken produced and flowback waters analyzed in this study were found to have total Ra activities (^{228}Ra + ^{226}Ra) up to 64 Bq/L and an average ^{228}Ra/^{226}Ra activity ratio of 0.45 (Table S6). ^{228}Ra/^{226}Ra activity ratios in the Bakken produced waters reported in this study are consistent with ratios reported for scale, sludge, and filter socks in North Dakota, with average ^{228}Ra/^{226}Ra activity ratios of 0.6, 0.3, and 0.4, respectively.[29]

Following a spill event, Ra retention to the sediments or soil can be obtained by (1) Ra adsorption to solids, and (2) Ra incorporation into secondary Ra-rich minerals (e.g., barite), which could result in accumulation of Ra in the soil and legacy of radium contamination in spill sites even after the brine has been removed.[30] The saturation index (SI) of minerals for both background and spill waters was modeled using PHREEQC software.[24] Using the chemical data obtained in this study, the model indicates that background waters in North Dakota are supersaturated with respect to aragonite, barite, calcite, and dolomite, and under-saturated with respect to gypsum (Table S8). The high concentrations of sulfate in the background surface water, as well as the high saturation state with respect to barite minerals (SI ∼ 1.5), suggests that Ra could precipitate out of solution with the formation of secondary barite minerals,[31] although no actual barite measurements in soil were conducted. Radium removal from spill water either by adsorption or coprecipitation with barite resulted in low activities of Ra in the spill water but elevated activities of Ra in the impacted soil (Figure 4).

In the Blacktail Creek spill, we found relatively low total Ra activities in the spill water itself (total Ra= 0.33 Bq/L) compared to the brines (up to 64 Bq/L), which is 190-fold lower radium activity, despite only the 8.5-fold dilution suggested by the chloride mass balance. The apparent Ra depletion in the spill water is consistent with highly elevated activities of total Ra and relatively lower ^{228}Ra/^{226}Ra activity ratios in the stream sediments (total Ra= 553−4684 Bq/kg;

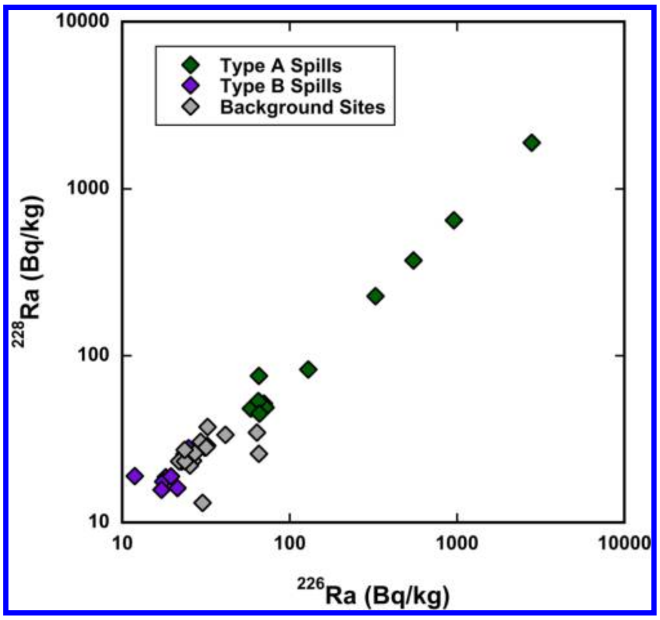

Figure 4. ^{228}Ra vs ^{226}Ra activities in sediments and soils from spill sites and away from spill areas in ND. The greatest accumulation of Ra in soils was found in the large magnitude spills of Bear Den Bay (3.8 million L) and the Blacktail Creek (11 million L) that are defined as type A spills. The high correlation of ^{228}Ra and ^{226}Ra and their ratio (~0.6) in the soils from the spill sites reflect the NORM composition of the Bakken brines and the relatively young age of the spills. Note the high accumulation of radium in the contaminated soil, several orders of magnitude greater relative to the radium level in soil from background sites.

^{228}Ra/^{226}Ra = 0.67–0.69), compared to upstream sediments (45 Bq/kg; 1.1). We also found elevated Ra activities and relatively low ^{228}Ra/^{226}Ra activity ratios in soil samples collected at the Bear Den Bay spill site (total Ra = 106–211 Bq/kg; ^{228}Ra/^{226}Ra = 0.64–0.82) compared to average background soils (58 Bq/kg; 0.85).

The effectiveness of Ra adsorption to sediment or soil depends on several factors such as the relative water to sediment ratio, water salinity, water chemistry (i.e., distribution of bivalent cations), soil type, cation exchange capacity (CEC) on clay minerals, organic matter content, oxide content, and grain size.[27,30,32,33] The high salinity of the Bakken brines may effectively inhibit Ra adsorption to the sediment or soil at the spill site itself; instead, Ra adsorption may be more effective downstream of the spill, when the brine becomes diluted with meteoric water. This phenomenon was observed in the Bear Den Bay site, where total Ra activities increased from ~100 Bq/kg at the original spill site to ~200 Bq/kg at approximately 0.4 km downstream from the original spill site (Figure S1). Parallel to the increase in total Ra activity, the ^{228}Ra/^{226}Ra activity ratios decreased with distance along the flow path of the spill water. We conclude that the impact of the high NORM in the Bakken brines will be reflected in accumulation of Ra in soil, indicated by elevated levels of total Ra and relatively lower ^{228}Ra/^{226}Ra activity ratios in soils and sediments from spill sites compared to background soils and sediments.

Environmental Implications of Brine Spills. In addition to elevated levels of salts, the Bakken brines contain elevated levels of trace elements and other toxic contaminants such as Ba (up to 9 mg/L), NH_4 (2,500 mg/L), Pb (3480 μg/L), Tl (231 μg/L), Cd (31 μg/L), Se (970 μg/L), Cu (365 μg/L), Ni (833 μg/L), V (1020 μg/L), and Mn (16 mg/L). Spill waters and surface waters impacted by spills identified in this study were found to have trace metal concentrations often 1 to 2 orders of magnitude greater than average concentrations in background surface waters (Table 2 and Figure 2). Additionally, these levels exceeded national ecological and drinking water regulations for multiple elements in some spill sites. Environmentally toxic selenium was measured in the majority of spill waters at elevated concentrations up to 172 μg/L, 35 times the National Recommended Criterion Continuous Concentration (CCC) for freshwater aquatic life (5 μg/L).[34] Likewise, high levels of NH_4 in spill waters (up to 42 mg/L) far exceed the US Environmental Protection Agency (EPA) acute and chronic ambient water quality criteria for protecting freshwater organisms from potential effects of Total Ammonium Nitrogen (TAN) of 17 mg/L and 1.9 mg/L, respectively (at pH = 7).[35] Additionally, certain elements were measured at concentrations above the National Maximum Contaminant Level (MCL) Drinking Water (Se, Tl, Ra) and Secondary Drinking Water (Cl, Fe, Mn) standards in some spill waters.[36] Given that spills can be located upstream from drinking water sources, as is the case in the Bear Den Bay spill, long-term monitoring of the waters downstream of spills is necessary in order to assess impacts on drinking water quality. Overall, our data show that the Bakken brines are enriched in numerous toxic elements and their release to the environment could directly affect the quality of the impacted water.

The results of this study indicate that the water contamination from brine spills is remarkably persistent in the environment, resulting in elevated levels of salts and trace elements that can be preserved in spill sites for at least months to years (up to 4 years for ND 128 and 129 samples) following the original spill. The concentrations of Br, V, Se, Li, B and Sr had strong linear correlations with Cl (Figure 2 and S4), which suggests that they behave conservatively and natural remediation is only due to dilution. Other constituents such as NH_4, SO_4, Ba and Mn, had ratios with Cl that are not consistent with those in the Bakken brines (Figure 2 and S6), and could reflect the retention of these elements to the soil or sediment at the spill sites or biological uptake. Additionally, we also observed the accumulation of long-lived isotopes of Ra in the sediments and soils of spill sites. The relatively long half-life of ^{226}Ra (~1600 years) suggests that Ra contamination in spill sites will remain for thousands of years.

The increase in the occurrence of brine spills in North Dakota parallels the rapid rise of unconventional oil production from tight oil in the Bakken region since 2007 (Figure 5). We found that the occurrence of brine spills in North Dakota is correlated with oil well density (Figure 1, Figure S7), indicating that areas of high oil well density are relatively more likely to be impacted by spills. Analysis of the ~3900 documented brine spills in North Dakota[16] shows that spills generally ranged in volume from 200 to 10000 L (Figure S8). Pipeline leaks made up 18% of the spill events and were responsible for 47% of the spilled water by volume. The spatial distribution of oil, gas, and brine pipelines is not currently available in the public domain at the resolution needed to accurately assess the spatial relationship between pipeline network distribution and spill occurrence. Following pipeline leaks were valve/piping connection leaks (20.5% of volume, 24.8% of frequency) and tank leaks and overflows (14.5% of volume, 22.4% of frequency) (Figure S9). In sum, we find that the release of

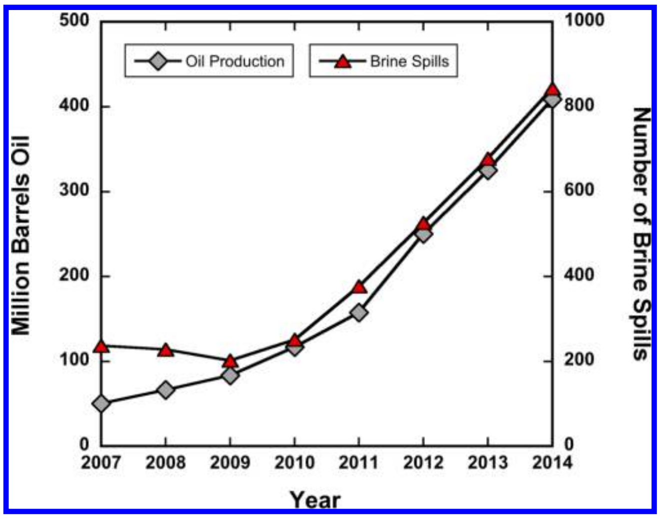

Figure 5. Graph depicting the parallel rise of annual Bakken oil production (×10^6 barrels) and number of brine spills in North Dakota from 2007 to 2014. Spill data were compiled from the North Dakota Department of Health.[16] Bakken oil production data were compiled from the Energy Information Administration.[38]

OGW to the environment since 2007 from accidental spills is largely due to infrastructure failures.

Overall, the establishment of the geochemical and isotopic ($^{87}Sr/^{86}Sr$) fingerprints of the Bakken brines enabled us to identify OGW spills, in spite of the highly saline background waters in areas of unconventional oil and gas development in North Dakota. The data show that, in addition to the high levels of dissolved salts such as Br and Cl, the spills are enriched in several contaminants such as NH_4, Se, V, B, and Mn relative to background water. The resistance of inorganic contamination to biodegradation and its consequential persistence in the environment suggest that contamination from brine spills in North Dakota will continue to impact nearby water resources for years to come. To fully understand the impacts of brine spills in North Dakota, future research should evaluate additional spill sites, analyze organic contamination in addition to inorganic elements, assess the impacts downstream of spill sites, including risks to drinking water sources, and conduct a comprehensive assessment of long-term ecological and possible human health impacts. The findings of this study are important for the identification of OGW in the environment and assessment of the environmental implications associated with OGW spills in other regions undergoing intense development of unconventional oil and gas infrastructure.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b06349.

Further information on the sampling techniques, sample site locations, and sample descriptions; additional figures and tables (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: (919) 681-8050. Fax: (919) 684-5833. E-mail: vengosh@duke.edu.

Notes

The authors declare no competing financial interest.

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