

Investigating the Mineral Potential of Brines in Saskatchewan: Results from the 2017 Field Season for the Brine Sampling Project

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Jensen, G.K.S. and Rostron, B.J. (2017): Investigating the mineral potential of brines in Saskatchewan: results from the 2017 field season for the brine sampling project; in Summary of Investigations 2017, Volume 1, Saskatchewan Geological Survey, Saskatchewan Ministry of the Economy, Miscellaneous Report 2017-4.1, Paper A-1, 6p.

Abstract

Formation brines are a source of industrial minerals and chemicals in some sedimentary basins around the world. In 2011, the Saskatchewan Geological Survey initiated a wellhead sampling project to obtain background information on the concentrations/amount and distribution/location of industrial minerals and chemicals in produced brines, to support the prospect of producing industrial minerals from brines. The goal of this project is to determine the distribution and concentration of the major and minor elements present in subsurface brines across Saskatchewan. In addition, routine chemical analysis of formation waters only measures major elements; the data collected on the minor elements in brines therefore represent some of the first publicly available data of this nature in the province.

This project commenced in 2011 with sampling of wells in southeastern Saskatchewan that produced from Lower Paleozoic formations. Sampling continued in other Paleozoic strata in 2012, 2013 and 2016. The latest round of sampling was in the summer of 2017, and included Paleozoic strata in southwestern Saskatchewan, along with a resampling of selected previously sampled wells to investigate whether there had been a change in the chemistry of the produced brine over time. The resampling was completed with the aim of demonstrating a consistent concentration of the target elements, which would ensure the long-term economic viability of an industrial mineral/chemical project.

The results presented in this paper augment the database of samples already publicly available on the Government of Saskatchewan website.

Keywords: industrial minerals, brine, geochemistry, Williston Basin, bromine, iodine, lithium, Duperow Formation, Birdbear Formation, Winnipegosis Formation

1. Introduction

Formation waters with a total dissolved solids (TDS) content greater than 100 000 milligrams per litre (mg/L) are termed brines (Carpenter, 1978). For the purpose of this paper, formation waters with less than 100 000 mg/L TDS but which are potentially sources of economic minerals, are also included. Brines present in the subsurface of Saskatchewan represent a possible new resource for the province and the companies that operate here. This is due to the possibility of these fluids possessing high concentrations of elements such as lithium, bromine and iodine, the production of which could provide revenue to help develop a brine industry in Saskatchewan. The Saskatchewan Geological Survey initiated a wellhead sampling program in 2011 to achieve a better understanding of the subsurface brines present in the province, as well as provide a publicly available database of the major and minor elements present in the brines throughout Saskatchewan. Since 2011, sampling has been carried out in 2012, 2013, 2016 and, most recently, in 2017 (Jensen, 2011, 2015, 2016). The sampling program in the summer of 2017 targeted wells in the southwestern part of the province. In addition, selected wells previously sampled in 2011, 2012 and 2016 were resampled to determine if there had been any significant changes in brine chemistry over the production history of the wells.

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Although brine data directly from oil and gas companies do exist, a large percentage of those data are contaminated by various means: either drilling fluid, completion fluids, multi-zone production intervals, or even out-of-zone formation fluid entering the well bore *via* compromised well casing. Furthermore, chemistry data from oil and gas wells routinely contain analyses for major dissolved elements (*e.g.*, chlorine, sodium, calcium and magnesium), but analyses for trace elements of economic interest are rarely completed. Previous research into the economic potential of formation brines by Kreis and Gent (1992) and Rostron *et al.* (2002), using mainly samples from drill stem tests (DST) and some wellhead samples, demonstrated the presence of economic minerals in brines from the subsurface of Saskatchewan.

Samples obtained directly from producing wellheads are preferred, to eliminate the presence of drilling, completion or stimulation fluids, thus decreasing the risk of contamination. Thus, for the sampling conducted as part of this project, all samples were collected from wellheads after sufficient time had elapsed after drilling to avoid encountering any work-over fluids.

2. Current Work

During the summer of 2017, samples were collected from nine wells producing from Devonian-aged formations (Figure 1): one in the Winnipegosis Formation, three in the Duperow Formation, and five in the Birdbear Formation. As well, one sample was collected from producing Mississippian-aged strata (Madison Formation; Figure 1). Sampling procedures have been described previously (Jensen, 2011, 2015).

Resampling of selected wells was completed to investigate whether the brine chemistry had changed over the production history (Jensen, 2016). Wells with high concentrations of lithium were targeted for resampling, as long as they were still operational. Three of the resampled wells are in the Birdbear Formation; two in Township 1, Range 16W2 (wells 7 and 8 on Figure 1) and one in Township 2, Range 19W2 (well 9 on Figure 1). The fourth resampled well is in the Winnipegosis Formation, in Township 2, Range 9W2 (well 10 on Figure 1).

3. Results

a) New Sampling

The objective of the 2017 sampling season was to include more wells in the western part of the province, including wells producing from formations not previously sampled. Three water-source wells completed into the Duperow Formation were operating in this region of the province in 2017; one of these wells was sampled in 2016.

Results of the formation water analyses are displayed in Table 1, with the sample interval provided for each well. A sample interval consisting of a single number indicates a horizontal well, and the total vertical depth (TVD) is reported as the sample interval. Values for total dissolved solids (TDS) range from 6280 to 308 900 mg/L. There is a variation in the TDS values in the formations that have multiple samples. Chloride and sodium are the elements with the highest concentrations in all samples, as expected (Kreis and Gent, 1992; Rostron *et al.*, 2002). Trace element data for lithium are highlighted in the following discussion because of its potential economic significance.

Two new samples were collected from the **Birdbear Formation** in the western part of the province, near the Alberta–Saskatchewan border (wells 5 and 6 on Figure 1). Despite the relative depth of this formation in the area, TDS values in these samples are relatively low, ranging from 26 700 to 27 600 mg/L. Lithium concentrations for the samples are correspondingly low, ranging from 3.6 to 5.0 mg/L.

One new sample was obtained from a well producing from the **Madison Formation** (well 4 on Figure 1). Despite the deeper production depth of 1491 to 1553 metres, the TDS value was a relatively low 6280 mg/L. A review of published TDS maps (Jensen *et al.*, 2015) reveals that, in this area, TDS concentrations in the Madison are low. The lithium concentration in the sample was only 1.3 mg/L, the lowest observed in the samples collected in 2017.

Finally, three samples from the **Duperow Formation** were obtained from the western region of the province (wells 1, 2 and 3 on Figure 1). The Duperow Formation is stratigraphically the deepest formation sampled in the area, and

brines had a TDS range of 198 800 to 284 200 mg/L. The corresponding lithium concentrations range from 36 to 78 mg/L. It is of interest, however, that two of the samples have values of 70 and 78 mg/L (from wells 01/03-27-032-23W3 and 31/04-20-032-23W3, respectively), which are more than double the value in well 01/09-10-026-19W3 (36 mg/L). This apparent anomaly is discussed below in 'Interpretation of Newly Sampled Wells'. These lithium concentrations are the highest in the samples obtained in 2017, as well as some of the highest obtained in the five years of sampling.

b) Resampling

Results from 2017 for the resampled wells are displayed in Table 2, along with results from previous years. Lithium concentrations have remained relatively consistent through time for each well. TDS values are similar between the three sampling intervals, with differences ranging from 15 900 to 28 600 mg/L. However, variations are all less than 10% of the TDS, and most are less than 5% of the TDS, well within the analytical margin of error of saline brine samples.

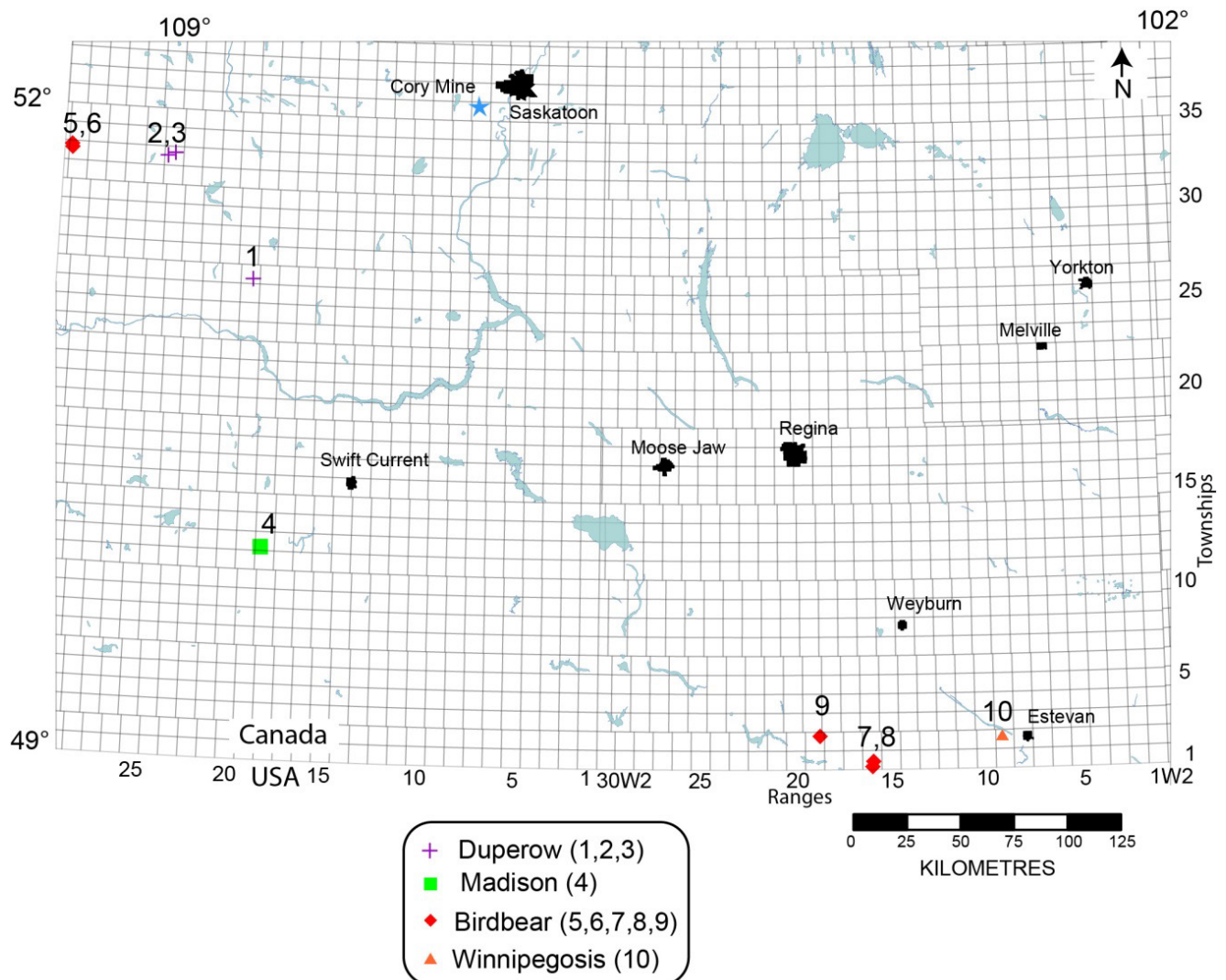


Figure 1 – Locations of wells from which wellhead samples were obtained in the summer of 2017. Numbers in brackets after formation names in legend refer to well numbers shown on figure.

Table 1 – Results* for formation water analyses for samples collected in the summer of 2017. All concentrations are in milligrams per litre (mg/L). Values that are reported as “bdl” indicate that elemental concentration was below detection limit. UWI = Unique well identifier.

Well No. on Fig. 1	UWI	Formation	Licence No.	Sample Interval (metres)	Collection Date	Sample Location Lat./Long.		Sample Location UTM		Detection Limit															TDS	pH		
						Longitude NAD27	Latitude NAD27	Easting NAD83 Zn13	Northing NAD83 Zn13	0.2	0.002	0.01	0.2	0.01	2	0.02	0.001	0.2	0.9	0.4	0.01	0.001	0.01	0.2			5	0.9
										Ba	B	Br	Ca	Cl	Fe	Pb	Li	Mg	Mn	K	Na	Sr	Th	Zn			HCO ₃	SO ₄ **
1	01/09-10-026-19W3	Duperow	53769	1258 to 1403	Summer 2017	-108.5657	51.20662	250897.0482	5678851.982	0.74	77	1177	24 900	183 000	bdl	0.04	36	4610	bdl	5780	74 900	780	bdl	1.6	544	800	284 200	5.96
2	01/03-27-032-23W3	Duperow	84L222	1089 to 1097	Summer 2017	-109.18399	51.76705	211290.0966	5743421.442	bdl	61	405	7820	128 000	bdl	bdl	70	2240	bdl	5530	62 500	219	0.013	bdl	1160	1130	198 800	5.85
3	31/04-20-032-23W3	Duperow	14F071	1134	Summer 2017	-109.23778	51.75338	207492.0294	5742116.592	bdl	61	393	7800	137 000	bdl	bdl	78	2010	bdl	5910	69 600	218	bdl	bdl	1020	1040	215 600	5.83
4	31/02-08-012-18W3	Madison	99J205	1491 to 1553	Summer 2017	-108.4246	49.97772	254434.4304	5541780.578	bdl	4.6	1.2	499	492	bdl	bdl	1.3	147	bdl	61	1330	12	bdl	bdl	275	3450	6280	7.14
5	21/04-29-032-28W3	Birdbear	12D286	937	Summer 2017	-109.94759	51.76549	158622.4582	5746551.144	bdl	13	56	519	14 200	bdl	bdl	5	258	bdl	150	9200	24	bdl	bdl	684	600	26 700	7.55
6	11/01-31-032-28W3	Birdbear	13B260	935 to 940	Summer 2017	-109.95172	51.78008	158448.0373	5748191.784	bdl	9	57	677	13 800	bdl	bdl	3.6	313	2	96	9170	22	bdl	bdl	240	4800	27 600	6.87
7	31/13-03-001-16W2	Birdbear	98A022	2404 to 2430	Summer 2017	-104.07324	49.01323	567732.3763	5429344.569	5.86	353	534	11 500	166 700	3	0.09	29	1300	3	3740	93 300	626	bdl	0.6	5	630	278 700	3.63
8	11/11-15-001-16W2	Birdbear	97L060	2407 to 2429	Summer 2017	-104.06629	49.03712	568207.9133	5432006.509	8.21	394	547	13 400	174 500	10	bdl	37	1500	bdl	4090	97 400	727	bdl	0.48	46	600	292 900	5.22
9	01/10-26-002-19W2	Birdbear	66G047	2306 to 2326	Summer 2017	-104.44044	49.15422	540765.2322	5444755.025	2.49	278	389	7170	147 600	bdl	bdl	44	910	bdl	3100	85 400	354	bdl	0.3	188	690	246 100	6.47
10	11/08-22-002-09W2	Winnipegosis	86A105	2575 to 2584	Summer 2017	-103.12102	49.1356	637024.0474	5444234.264	12.4	108	380	11 200	186 000	bdl	bdl	47	1100	bdl	5229	99 900	468	0.04	1.2	99	158	308 900	5.86

*The following elements were also analyzed but all were below their respective detection limit and are therefore not included in the table: aluminum (Al), antimony (Sb), arsenic (As), beryllium (Be), bismuth (Bi), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), molybdenum (Mo), nickel (Ni), selenium (Se), silicon (Si), silver (Ag), tin (Sn), titanium (Ti), uranium (U), vanadium (V).

When sample interval is only one number the well is horizontal and the total vertical depth (TVD) is reported as the sample interval.

**[SO₄] is calculated from [total S] by factor 96.06/32.06. This assumes all S exists as SO₄, and may slightly overestimate SO₄ concentrations.

Element abbreviations: Ba - barium, B - boron, Br - bromide, Ca - calcium, Cl - chloride, Fe - iron, Pb - lead, Li - lithium, Mg - magnesium, Mn - manganese, K - potassium, Na - sodium, Sr - strontium, Th - thallium, Zn - zinc.

Table 2 – Results* for formation water analyses for resampled wells. Alternating colours of rows correspond to matching well locations. All concentrations are in milligrams per litre (mg/L). Values that are reported as “bdl” indicate that elemental concentration was below detection limit. UWI = Unique well identifier.

Well No. on Fig. 1	UWI	Formation	Sample Interval (metres)	Collection Date	Detection Limit																			TDS	pH		
					0.04	0.2	0.002	0.01	0.002	0.2	0.01	2	0.02	0.001	0.2	0.9	0.4	9	0.01	0.001	0.01	0.09	0.2			5	0.9
					As	Ba	B	Br	Cd	Ca	Cl	Fe	Pb	Li	Mg	Mn	K	S	Na	Sr	Th	Ti	Zn			HCO ₃	SO ₄ **
7	31/13-03-001-16W2	Birdbear	2404 to 2410	Summer 2011	bdl	7.2	323	516	bdl	12 600	191 000	2.2	bdl	31	1500	bdl	4150	10	96 000	602	0.02	bdl	0.4	100	394	307 300	6.04
7	31/13-03-001-16W2	Birdbear	2404 to 2430	Summer 2016	bdl	7.06	403	536	bdl	11 700	170 100	bdl	0.04	41	1380	1.10	3880	bdl	92 600	612	0.02	bdl	0.82	77	480	281 800	5.63
7	31/13-03-001-16W2	Birdbear	2404 to 2430	Summer 2017	bdl	5.86	353	534	bdl	11 500	166 700	3.00	0.09	29	1300	3.00	3740	bdl	93 300	626	bdl	bdl	0.60	5	630	278 700	3.63
8	11/11-15-001-16W2	Birdbear	2407 to 2413	Summer 2011	0.80	8.4	316	498	bdl	14 000	192 000	6.7	bdl	33	1600	bdl	4290	bdl	98 500	720	0.02	0.1	0.5	93	180	312 300	5.99
8	11/11-15-001-16W2	Birdbear	2407 to 2429	Summer 2016	bdl	7.78	368	536	0.01	12 800	175 200	bdl	0.07	36	1400	1.00	4010	bdl	95 500	753	0.02	bdl	0.72	58	600	291 300	5.52
8	11/11-15-001-16W2	Birdbear	2407 to 2429	Summer 2017	bdl	8.21	394	547	bdl	13 400	174 500	10.0	bdl	37	1500	bdl	4090	bdl	97 400	727	bdl	bdl	0.48	46	600	292 900	5.22
9	01/10-26-002-19W2	Birdbear	2306 to 2326	Summer 2011	0.54	2.9	264	535	bdl	7680	160 000	bdl	bdl	48	1000	bdl	3320	10	88 600	325	bdl	0.1	bdl	200	647	262 700	6.63
9	01/10-26-002-19W2	Birdbear	2306 to 2326	Summer 2016	bdl	2.69	293	374	0.02	6900	147 700	bdl	bdl	52	890	bdl	3090	12	86 300	378	0.013	bdl	1.71	186	660	246 800	6.34
9	01/10-26-002-19W2	Birdbear	2306 to 2326	Summer 2017	bdl	2.49	278	389	bdl	7170	147 600	bdl	bdl	44	910	bdl	3100	bdl	85 400	354	bdl	bdl	0.30	188	690	246 100	6.47
10	11/08-22-002-09W2	Winnipegosis	2575 to 2584	Summer 2012	0.61	13.0	111	398	bdl	10 700	182 000	bdl	bdl	54	1000	bdl	4990	bdl	92 900	448	0.035	0.2	0.4	230	616	293 500	6.87
10	11/08-22-002-09W2	Winnipegosis	2575 to 2584	Summer 2016	bdl	14.8	147	438	bdl	12 100	189 400	bdl	0.03	63	1180	bdl	5680	10	101 000	519	0.04	bdl	1.20	98	360	311 000	6.28
10	11/08-22-002-09W2	Winnipegosis	2575 to 2584	Summer 2017	bdl	13.4	108	380	bdl	11 200	186 000	bdl	bdl	47	1100	bdl	5230	bdl	99 900	468	0.04	bdl	1.20	99	158	308 900	5.86

*The following elements were also analyzed but all were below their respective detection limit and are therefore not included in the table: aluminum (Al), antimony (Sb), beryllium (Be), bismuth (Bi), chromium (Cr), cobalt (Co), copper (Cu), molybdenum (Mo), nickel (Ni), selenium (Se), silver (Ag), tin (Sn), uranium (U), vanadium (V).

**[SO₄] is calculated from [total S] by factor 96.06/32.06. This assumes all S exists as SO₄, and may slightly overestimate SO₄ concentrations.

Element abbreviations: As - arsenic, Ba - barium, B - boron, Br - bromide, Cd - cadmium, Ca - calcium, Cl - chloride, Fe - iron, Pb - lead, Li - lithium, Mg - magnesium, Mn - manganese, K - potassium, S - silicon, Na - sodium, Sr - strontium, Th - thallium, Ti - titanium, Zn - zinc.

4. Interpretation of Newly Sampled Wells

The three Duperow Formation samples from 2017 are located approximately 50 kilometres from one another (Figure 1). It was expected that the samples would have a similar chemistry as the wells are all relatively close together, on a basin scale. Indeed, samples from wells 01/03-27-032-23W3 and 31/04-20-032-23W3 (wells 2 and 3 on Figure 1) do have similar chemistry (Table 1). The sample from well 01/09-10-026-19W3 (well 1 on Figure 1) is anomalous, however, with an elevated bromide concentration compared to the two other Duperow samples (1177 mg/L, compared to 405 and 393 mg/L). This concentration of bromide is more than double that of the other values obtained in the 2017 sampling season (Table 1). Analysis of this sample was repeated by the laboratory, and remained consistent, ruling out possible analytical error. A review of the production interval on well 01/09-10-026-19W3 reveals that the production zone (1258 to 1403 m) is both larger and ultimately deeper than the other Duperow wells (1089 to 1097 m for well 01/03-27-032-23W3, and a TVD of 1134 m for well 31/04-20-032-23W3). It is very likely that the well at 01/09-10-026-19W3 is producing from both the Duperow Formation and the underlying Souris River Formation. Elevated levels of bromide (*i.e.*, >700 mg/L) have been observed previously from the Souris River Formation elsewhere in the province (Jensen *et al.*, 2006). Shaft inflows from the Souris River Formation at the Cory potash mine near Saskatoon (blue star on Figure 1) display bromide concentrations ranging from 691 to 995 mg/L. As the Souris River Formation lies directly below the Duperow at well 01/09-10-026-19W3, this accounts for the elevated bromide value in the sample from this location, as well as the decreased lithium concentration compared to the samples from the other nearby Duperow wells (36 mg/L, compared to 70 and 78 mg/L). The knowledge that the underlying Souris Valley Formation is enriched in bromide and depleted in lithium respective to the Duperow Formation will potentially aid operators with drilling and completion techniques when drilling for brine-producing wells.

The Birdbear Formation samples in the northwestern part of the study area (wells 21/04-29-032-28W3 and 11/01-31-032-28W3; wells 5 and 6 on Figure 1) display low levels of lithium (5.0 and 3.6 mg/L, respectively; Table 1), as well as a low TDS. When compared to the Birdbear samples from the southeastern part of the study area (31/13-03-001-16W2, 11/11-15-001-16W2 and 01/10-26-002-19W2; wells 7, 8 and 9 on Figure 1), it is evident that there is a spatial variation within the Birdbear Formation within the province, likely a result of the brine's evolution. For the Birdbear Formation, results to date suggest that the southeastern region of the province hosts a better potential for lithium production than the western region.

5. Discussion of Resampled Wells

Lithium concentrations are generally similar between the wells resampled in 2017, ranging from 29 to 47 mg/L, and those sampled in previous years, which ranged from 31 to 63 mg/L (Table 2).

When comparing major elements (Cl, Na, Ca, K), all concentrations show a slight variance over the sampling interval (Table 2). This variance of some elements increasing and some elements decreasing in concentration is anomalous.

Possible interpretations for this variance in TDS, lithium and major element concentrations include:

- There could have been a change in the chemistry of the formation waters since the wells were first sampled.
- As the lithium content comprises such a small percentage of the total TDS (~0.02%) in the samples analyzed, the accuracy of the analytical method could be a factor in the variance present in the results.
- Two of the wells sampled, 31/13-03-001-16W2 and 11/11-15-001-16W2, both Birdbear Formation wells, were perforated at a lower depth in 2011. This lower production zone, which is still within the Birdbear Formation, could result in a change in the chemistry. After sampling these wells twice since the production zone changed (in 2016 and again in 2017) it is evident there has not been a significant change in the chemistry. Additionally, as the other Birdbear Formation wells did not change production zone and display similar variance in chemistry, it is the interpretation of the authors that in this case the change in production depth is not a factor in the changing chemistry. Yet it remains a possibility that there are variations in chemistry within formations; further sampling would be required to determine if such variation exists.

6. Future Work

The next step is to sample core from wells that display high lithium concentrations, to determine if the high lithium values in the brines can be attributed to the rock framework. Cores from the Duperow Formation will be the first priority, followed by cores from the Winnipegosis Formation. The first phase of this project will commence in 2018, with the results published in a *Summary of Investigations* paper by early 2019.

The two Duperow Formation wells in the western region of the province (01/03-27-032-23W3 and 31/04-20-032-23W3) display promising economic potential, as they possess a relatively high concentration of lithium (70 and 78 mg/L, respectively), and a low TDS value (198 800 and 215 600 mg/L). Additionally, the wells are shallower, typically by 1000 metres, than the other wells that have similar lithium concentrations. This shallow depth would decrease drilling costs for companies looking to produce lithium from the brines. If more wells are drilled into the Duperow Formation in the province, it will be a priority for this project to sample them.

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