GS2017-16

Preliminary investigation of the potential for lithium in groundwater in sedimentary rocks in southwestern Manitoba

by M.P.B. Nicolas

In Brief:

- Salinities in Manitoba's complex groundwater aquifer system range from brines in deeper aquifers to freshwater in shallower aquifers
- Compiled archival water chemistry data indicate Li is rarely analysed
- The highest Li value (7.32 ppm) was obtained from the Souris Valley aquifer

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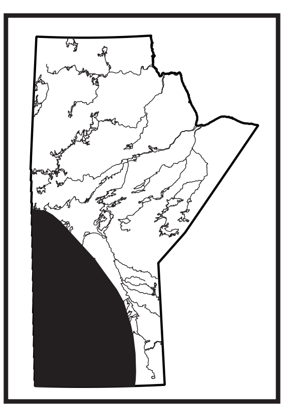

Summary

Production of lithium (Li) from deep brines in continental sedimentary basins is the most common and cost-effective source of Li. Southern Manitoba has a complex groundwater aquifer system, with salinities ranging from brines in the deeper aquifers to freshwater in the shallower and eastern aquifers. Manitoba's oil and gas operations produce large quantities of these brines, which contain a wide range of trace elements. Although very limited preliminary results indicate the Li concentrations in Manitoba's brines are low, extrapolation of better, more comprehensive results from Saskatchewan suggests that there is potential for Li concentrations to be higher than currently recorded in Manitoba and that more work needs to be done to evaluate the deeper aquifers.

This project seeks to evaluate the current level of knowledge of Li concentration in the deep brines, as well as the freshwater aquifers, to develop a better understanding of the mineral potential of brines in southern Manitoba. This paper reviews archival Li data from the literature and well records.

Introduction

Brines are accumulations of saline groundwater that occur in continental sedimentary basins and can be a common source of dissolved trace metals, including Li. Metal extraction from these deep brines through evaporitic methods is currently the most common and economical way of extracting Li (Munk et al., 2016). Typically, this extraction is carried out by pumping the brines to the surface and metal concentration occurs by evaporation in a succession of artificial ponds, each subsequent one in the circuit having a greater Li concentration. Depending on the climate, but typically after a few months to about a year, a concentrate of 1 to 2% Li is further processed in a chemical plant to yield various end products, such as lithium carbonate and lithium metal (Bradley et al., 2013). When produced from brines, Li has an economical threshold of approximately 100 ppm from a maximum depth of 1 km (Munk et al., 2016), making that method much more cost-effective than extracting the Li from hard-rock sources (e.g., spodumene from Li-bearing pegmatite). However, all brine operations to date rely on hot, arid climates at the extraction site as a means to evaporate and concentrate the brines, which can be a lengthy process. Other technologies are being tested in order to reduce the amount of time typically needed in traditional evaporation ponds (i.e., from 18 months to 1 day; JWN Energy Group, 2017).

With the demand for Li increasing, particularly for use in batteries for hybrid cars and portable electronic devices (Munk et al., 2016), continental brines in untraditional climates are being looked at as possible sources and their production is only limited by the technology currently available to extract the elements. Most Li brines are associated with sodium chloride evaporite deposits, of which there is an abundance in the Williston Basin. Information on trace elements in brines in Manitoba is scarce and, with global demand increasing for Li, the Manitoba Geological Survey is addressing the growing need for this basic geoscience information. The objectives of this project are to 1) search available archival groundwater-chemistry databases and well files for trace elements, including Li, in the sedimentary rocks in southern Manitoba; and 2) collect and analyze new groundwater samples for trace elements, including Li, with the purpose of providing a better understanding of the mineral potential of brines in southern Manitoba. This paper reports on results of the archival data search.

Regional setting

In Manitoba, the Williston Basin consists of Paleozoic, Mesozoic and Cenozoic strata that form a basinward, southwesterly-dipping wedge of carbonate, evaporite and clastic rocks (Nicolas, 2008; Nicolas and Barchyn, 2008). The Williston Basin is an intracontinental basin with potentially economic brines, as demonstrated by several groundwater aquifers hosted in sedimentary rocks with varying salinities and chemical signatures (Betcher et al., 1995; Grasby and Betcher, 2002; Palombi, 2008). This sedimentary package can range from a maximum thickness of approximately

2300 m in the extreme southwestern corner of the province to a few metres along its eastern outer edge (Nicolas and Barchyn, 2008). Within those strata are up to 16 separate regional aquifers, as defined by Palombi (2008), all with varying salinities (Figure GS2017-16-1). In the west, the Jurassic and Paleozoic aquifers are dominantly brines, with total dissolved solids (TDS) levels >35 000 mg/L, based on the classification system of Hem (1985); in the east, the Paleozoic aquifer, referred to as the carbonate-rock aquifer (Grasby and Betcher, 2002), is dominantly freshwater, with a TDS level <2000 mg/L. Narrow transition zones of saline to brackish water occur between these two end members; saline water has TDS levels between 10 000 and 35 000 mg/L, and TDS levels of brackish water range from 2000 to 10 000 mg/L (Hem, 1985). Figure GS2017-16-1 shows the variation in salinity from west to east.

The regional flow system is characterized by influx of freshwater from the topographic highs in the northwestern United States, at the western edge of the Western Canada Sedimentary

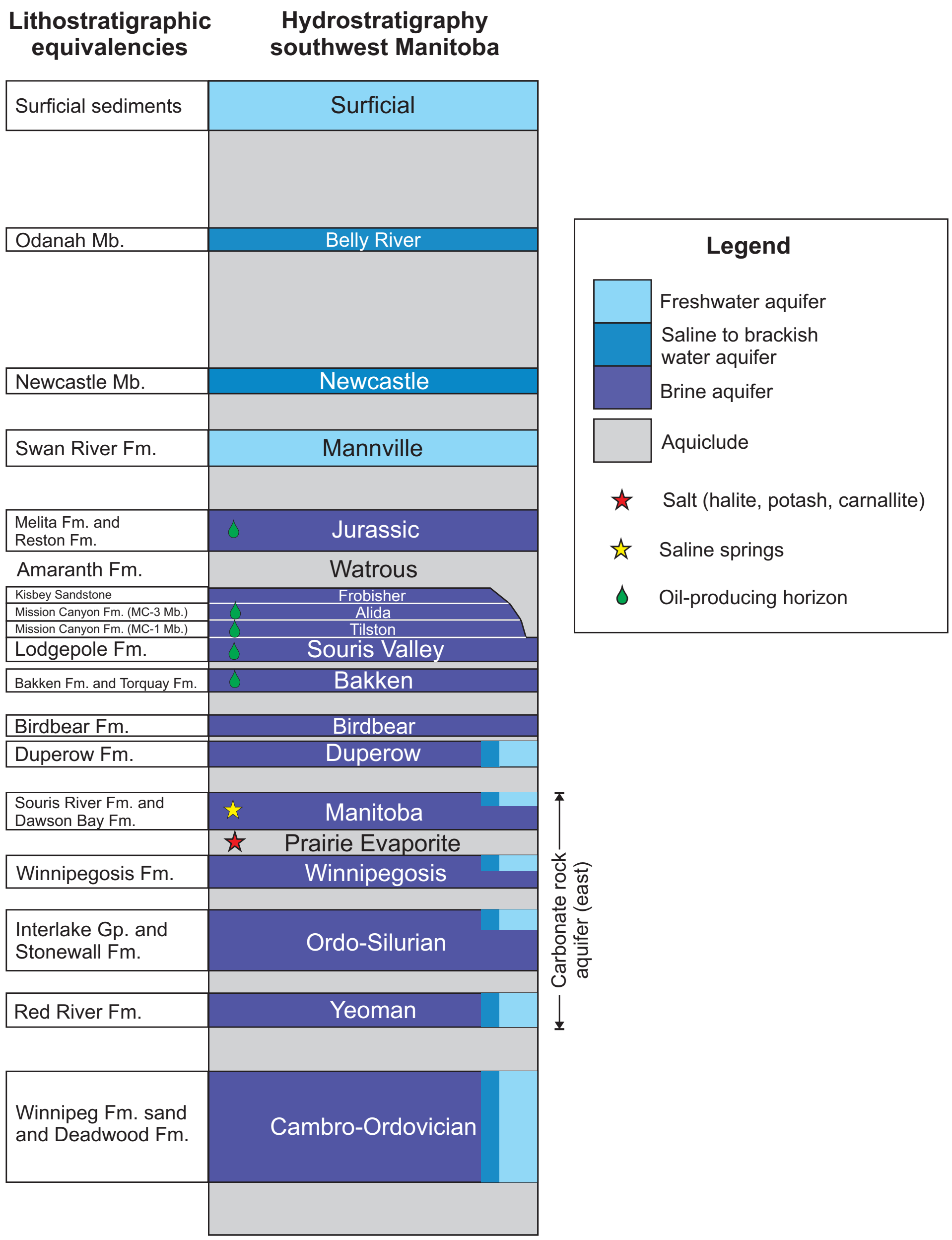

***Figure GS2017-16-1:** Hydrostratigraphy of southwestern Manitoba, modified from Palombi (2008), with equivalent southwestern Manitoba lithostratigraphic units. Red star indicates formation consisting dominantly of raw salt dominated by halite, potash and carnallite. Yellow star indicates formation with saline springs at surface. Horizons with oil production in Manitoba are indicated. The carbonate-rock aquifer range is as defined by Grasby and Betcher (2002). Aquifer-salinity changes are indicated by colour gradients; full-height boxes indicate salinity changes occur east- and northward, half-height boxes indicate salinity changes occur northward only. Salinity ranges are based on the classification of Hem (1985), and the total dissolved solids mapping of Palombi and Rostron (2013). Abbreviations: Fm., Formation; Gp., Group; Mb., Member.*

Basin (WCSB), with a regional movement of formation water to the northeast resulting in a western regional-scale updip flow of saline water into Manitoba. In Manitoba, saline springs discharge along the eastern edge of the Williston Basin located in the eastern part of the WCSB (van Everdingen, 1971; Downey et al., 1987; Hannon, 1987; Plummer et al., 1990; Bachu and Hitchon, 1996; Grasby and Betcher, 2002). Within the Williston Basin, host to several thin evaporitic beds, the Devonian Prairie Evaporite is the thickest evaporitic unit, reaching up to 200 m in thickness (Fuzesy, 1984; Yang et al., 2009), as well as the most widespread. This unit consists dominantly of salt, including halite, potash and carnallite, with minor anhydrite and clay (Nicolas, 2015). The subsurface distribution of the Prairie Evaporite can be seen in Fuzesy (1984), Bezys and Conley (1998), TGI Williston Working Group (2008) and Nicolas (2015). The regional flow system provides less saline waters from the southwest, and as water driving forces push the waters deeper into the basin and to the northeast, they cause them to mix with in situ formation waters. These waters partially or completely dissolve the Prairie Evaporite in its path, further increasing the salinity of the groundwater. In the east, the regional flow trend is reversed along the eastern erosional edge of the basin in the Interlake and Sandilands regions, where freshwater flows from east to west (Figure GS2017-16-2; Simpson et al., 1987; Betcher et al., 1995). This eastern freshwater system is referred to as the carbonate-rock aquifer and consists of gently west-dipping, carbonate-dominated strata spanning from the Red River Formation up to the Souris River Formation, and includes minor shales and evaporites (Grasby and Betcher, 2002). A major hydrological divide separates these two regional groundwater-flow systems (Figure GS2017-16-2; Grasby and Betcher, 2002). Saline springs occur west of this divide, where deep basinal waters flow updip to the surface (Figure GS2017-16-2).

Salt water production from oil wells

The Williston Basin in southwestern Manitoba is host to oil, gas, potash and salt resources. Oil and gas extraction are the dominant resource extraction industry in this part of the province, with minor salt extraction through solution mining. Potash resources, although extensive, have yet to be extracted (Nicolas, 2015). Through all these extraction processes, a large volume of saltwater (mostly brine, but can include saline or brackish water) is produced that requires treatment before being disposed of at various stratigraphic levels in the subsurface. This saltwater waste contains dissolved trace elements that may be of economic value.

Water production associated with oil and gas extraction is normal, and requires treatment and disposal after separation at oil batteries. The economics of any given oil well is not only dependent on the market oil price, but also on the oil/water ratio of that well during its lifetime, with water production increasing over time. Wells with higher water production (usually mature, long-producing wells) are more expensive to operate due to the logistics and costs associated with saltwater disposal. The hydrogeochemistry of the saltwater is variable, depending on the source formation and location within the basin. In Manitoba, deeper formation water is brine, with decreasing salinity toward the outcrop edge of the formation. Based on the mapping by Palombi (2008), water in subcropping formations shows a slight decrease in salinity toward the formations' erosional edge (Figure GS2017-16-1), but mostly is classified as brine. If the brines have dissolved metals at a considerable concentration, then this could assist in the economics of marginal wells.

Southwestern Manitoba has thousands of producing oil wells, all of them producing saltwater along with oil. The current oil producing horizons in Manitoba span from the Devonian Torquay Formation up to the Jurassic Melita Formation (Figure GS2017-16-1). Much of the produced water is re-injected into the producing formation from which it was extracted to assist with enhanced oil recovery (EOR) operations, with the added benefit that the water is already chemically compatible with the reservoir. Saltwater from wells that produce water in excess of what is needed for EOR, or that is simply not required, needs to be disposed of, which is generally done by injecting it into other deep formations within an aquifer that will not adversely affect other local groundwater systems or extractive operations. This excess saltwater may contain economic concentrations of dissolved trace elements, including Li.

Despite the high number of oil wells, data on trace-element contents from produced saltwater are limited because petroleum companies do not require this information for their operations. Water analyses that are conducted by petroleum companies are most often restricted to basic water-analysis packages offered by analytical laboratories. As a result, water analyses in petroleum technical well files usually report only on these major ions: K, Na, Ca, Mg, Fe, Cl, HCO_3, SO_4 and CO_3. Other dissolved metals may be measured upon request from the company, such as Sr, Ba, Bo, and rarely Br and I, but overall trace-element analysis, either of the full suite or of selected elements, is not done.

Data sources and results

The oil industry, on occasion, collects water samples during drill-stem tests (DST) from producing wells, or at batteries, to conduct water analyses. These water analyses, along with any additional chemical analyses conducted, are submitted to the Government of Manitoba and stored in the database of Petroleum Technical Well files. In addition, there are two major regional groundwater studies that were conducted, each consisting of several sampling sites. Grasby et al. (1999) collected a total of 1156 water samples from various aquifers sourced from domestic wells and testholes, saline springs, oil wells and DST analyses. A large suite of elements were tested but Li concentrations were not reported by these authors. Ferguson et al. (2005) compiled groundwater chemistry data from various sources, including Grasby et al. (1999), but focused only on results from the Winnipeg Formation aquifer (Cambro-Ordovician). Ferguson et al. (2005) results comprised concentrations for Li, including previously unreported results from the study conducted by Grasby et al. (1999). Table GS2017-16-1 shows

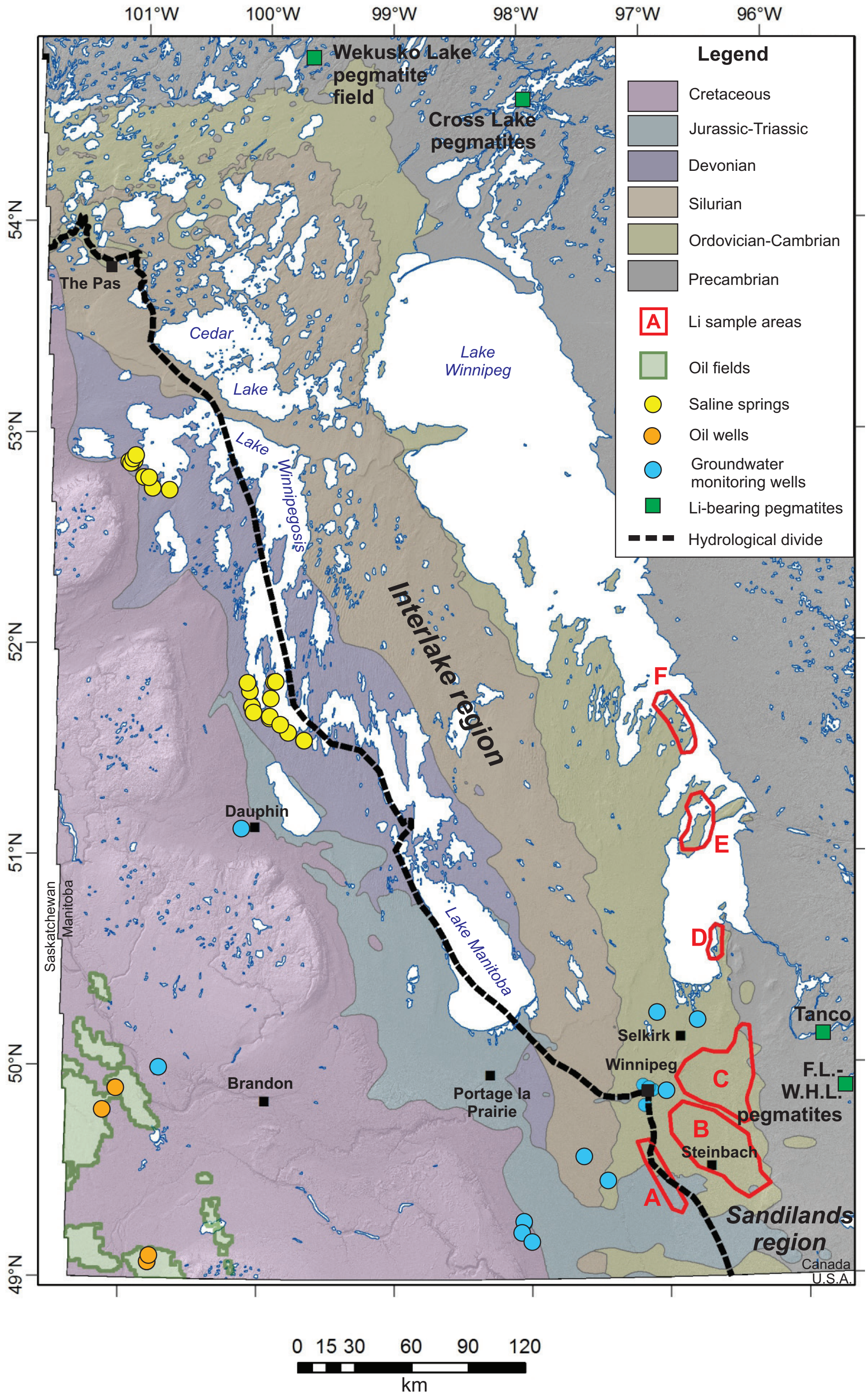

Figure GS2017-16-2: Regional geological map with digital elevation model of southern Manitoba showing hydrological divide (follows the 2000 mg/L total dissolved solids contour) with the location of saline springs and freshwater recharge regions from Grasby and Betcher (2002); areas A through F group multiple water-sampling points (data from Ferguson et al., 2005); oil wells and groundwater-monitoring wells with Li analyses are shown. Digital elevation model from United States Geological Survey (2002). Abbreviation: F.L.–W.H.L., Falcon Lake–West Hawk Lake.

Table GS2017-16-1: Lithium concentrations from selected Manitoba locations. All results are from groundwater analysis, except for the saltwater disposal well, which is measured from brine derived from a salt-solution operation. Licence numbers refer to the oil-well licence number. Water classification is based on Hem (1985). Areas A through F are as shown on Figure GS2017-16-2. Abbreviations: ABDP, abandoned producing well; Fm., Formation; Mb., Member; NA, not applicable; PTWF, Petroleum Technical Well File; SWD, saltwater disposal well; WSD, Water Stewardship Division.

Location	Well type	Stratigraphic unit or lithology	Depth (m)	Hydrostratigraphic unit	Water classification	Li (ppm)	Source
08-32-001-25W1 (licence 3311)	ABDP	Lower Amaranth Mb. (siltstone)	887.0-902.0	Jurassic aquifer	brine	3.970	PTWF
05-09-002-25W1 (licence 3492)	ABDP	Lower Amaranth Mb. (siltstone)	881.0-891.0	Jurassic aquifer	brine	0.258	PTWF
13-31-009-27W1 (licence 3138)	ABDP	Lodgepole Fm. (carbonate)	713.0-745.5	Souris Valley aquifer	brine	7.320	PTWF
03-12-011-27W1 (licence 4948)	SWD	Prairie Evaporite (salt)	1216.0-1299.0	Prairie Evaporite aquiclude	brine	< 1.800	PTWF
Area A	various	Winnipeg Fm.	NA	Cambro-Ordovician aquifer	saline and freshwater	0.000054-0.00115	Ferguson et al. (2005)
Area B	various	Winnipeg Fm.	NA	Cambro-Ordovician aquifer	freshwater	0.00001-0.170	Ferguson et al. (2005)
Area C	various	Winnipeg Fm.	NA	Cambro-Ordovician aquifer	brackish to freshwater	0.00003-0.300	Ferguson et al. (2005)
Area D	various	Winnipeg Fm.	NA	Cambro-Ordovician aquifer	freshwater	0.002-0.080	Ferguson et al. (2005)
Area E	various	Winnipeg Fm.	NA	Cambro-Ordovician aquifer	saline to freshwater	0.006-0.020	Ferguson et al. (2005)
Area F	various	Winnipeg Fm.	NA	Cambro-Ordovician aquifer	brackish to freshwater	0.005-0.190	Ferguson et al. (2005)
RIVER LOT UNKNOWN IN PARISH OF St. Boniface	observation	Winnipeg Fm. (sandstone)	172.935	Cambro-Ordovician aquifer	brine	3.440	WSD
RIVER LOT 0035 IN PARISH OF St. John	observation	Winnipeg Fm. (sandstone)	190.195	Cambro-Ordovician aquifer	brine	0.857	WSD
SW-4-11-4E	observation	carbonate	105.156	Carbonate rock aquifer	saline	0.780	WSD
NW-8-6-1E	observation	carbonate	36.576	Ordo-Silurian aquifer	saline	1.400	WSD
NW-13-7-2W	observation	carbonate	136.55	Ordo-Silurian aquifer	saline	0.488	WSD
NW-13-7-2W	observation	carbonate	136.55	Ordo-Silurian aquifer	saline	0.616	WSD
NE-1-15-3E	observation	sandstone	147.523	Cambro-Ordovician aquifer	saline	2.000	WSD
NE-30-14-6E	test well	sandstone	89.611	Cambro-Ordovician aquifer	saline	3.230	WSD
SW-6-3-4W	observation	sandstone	86.563	Jurassic aquifer	saline	1.560	WSD
SW-6-3-4W	observation	sandstone	86.563	Jurassic aquifer	saline	1.330	WSD
SW-6-3-4W	observation	sandstone	86.563	Jurassic aquifer	saline	1.280	WSD
SW-6-3-4W	observation	sandstone	86.563	Jurassic aquifer	saline	1.200	WSD
SW-22-3-5W	observation	sandstone	96.926	Jurassic aquifer	saline	0.949	WSD
SW-22-3-5W	observation	sandstone	96.926	Jurassic aquifer	saline	1.470	WSD
SW-22-3-5W	observation	sandstone	96.926	Jurassic aquifer	saline	1.030	WSD
NW-35-3-5W	observation	sandstone	71.628	Jurassic aquifer	saline	0.761	WSD
NW-35-3-5W	observation	sandstone	71.628	Jurassic aquifer	saline	1.380	WSD
NW-35-3-5W	observation	sandstone	71.628	Jurassic aquifer	saline	1.140	WSD
RIVER LOT 0035 IN PARISH OF St. John	production	carbonate	NA	Carbonate rock aquifer	brine	3.840	WSD
NW-8-12-24W	observation	shale	27.45	Belly River aquifer?	saline	1.180	WSD
SE-12-25-20W	production	shale	39.65	Belly River aquifer?	saline	0.706	WSD
RIVER LOT 0015 IN PARISH OF St. Vital	test well	Winnipeg Fm. (sandstone)	158.6	Cambro-Ordovician aquifer	saline	0.958	WSD

the range in Li concentrations reported in Ferguson et al. (2005) grouped by geographic area (also shown in Figure GS2017-16-2). Another source of water-chemistry data is from groundwater monitoring and test wells from the internal database GWDrill managed by the Water Stewardship Division of Manitoba Sustainable Development (Table GS2017-16-1; Manitoba Water Stewardship, 2007). Although restricted to shallower (<200 m) aquifers, it provides information on different aquifers and complements data collected by Grasby et al. (1999) and Ferguson et al. (2005).

The search through the Petroleum Technical Well files returned only four well records with Li concentrations reported (Table GS2017-16-1). Due to the high number of well records, a strategic search was conducted focusing on 1) wells with chemical analyses indexed in the well files; 2) wells with water analyses indexed in the well files that are either water-source wells or saltwater-disposal wells (abandoned or active); and 3) random sampling of producing or abandoned dry wells. Of the four well records, only three represent samples from the groundwater itself, and the fourth is from brine from a salt-solution operation in the Prairie Evaporite.

Comparison to brines in Saskatchewan

Saskatchewan extracts oil from deeper horizons than that produced in Manitoba, allowing for a wider range of aquifers to be easily tested at the oil-well sites. As a result, the deep aquifers in the Saskatchewan portion of the Willison Basin have undergone more testing for trace-metals concentrations, including Li. Rostron et al. (2002) report on the Saskatchewan Brine Sampling Program, which collected formation water from several deep aquifers. Follow-up work was conducted by Jensen (2011, 2012, 2016). Rostron et al. (2002) reported Li values from southeastern Saskatchewan as high as 112 ppm from the Yeoman aquifer, 108 and 83.7 ppm from the Duperow aquifer, whereas Jensen (2012, 2016) reported subeconomic Li values, the highest being 59.0 ppm, from the Birdbear aquifer and 63 ppm from the Winnipegosis aquifer.

Discussion

The concentration of Li in Manitoba's groundwater is variable, with values from brines in the oil wells ranging from 0.258 to 7.320 ppm; values from freshwater to brackish water wells ranging from 0.00001 to 0.300 ppm; and values from shallow saline waters to brines in monitoring wells ranging from 0.488 to 3.840 ppm (Table GS2017-16-1). Despite the small number of results from deep brines, Li concentrations in Manitoba's groundwater are low, with overall higher concentrations in the deep Jurassic and Paleozoic brines of southwestern Manitoba's oil region. Shallower brines and saline waters measured from the groundwater monitoring wells have slightly lower values for Li, compared with the brines derived from deep oil wells (Table GS2017-16-1). Freshwater-dominated Cambro-Ordovician aquifers along the eastern erosional edge of the Williston Basin have extremely low Li concentrations, likely just within detection limits.

The Li values in Table GS2017-16-1, regardless of the source, do not meet the economic threshold used for current evaporitic extraction methods (Munk et al., 2006), notwithstanding the fact that the climate in Manitoba is not suitable for open-air evaporation ponds. Although Li extraction from the brines is generally more promising than extraction from the freshwater in Manitoba's groundwater column, extracting this element can only be considered with the help of new low-cost, efficient technologies that would be capable of treating the brine on site, such as at oil batteries and saltwater source or disposal sites. Such technologies are currently being developed by MGX Mineral Inc., where a new low-energy design, rapid-recovery process is being tested with promising results (MGX Minerals Inc., 2017). This type of technology could also be used in Manitoba if it can be developed for application in commercial-scale operations.

Given that Saskatchewan reports higher Li concentrations in deeper horizons than those tested in Manitoba and the regional groundwater flow is to the east and northeast (Figure GS2017-16-2), there is the possibility that higher Li concentrations can also be found in Manitoba. More testing would need to be done to verify this hypothesis but given the current oil production, testing would be limited to the restricted oil column currently in production and the deeper horizons (e.g., Red River and Duperow formations) could not be tested, unless wells deeper than those reaching the current oil-producing horizons were drilled.

Lithium concentrations in the Cambro-Ordovician freshwater aquifer, despite being low, are quite variable. Of all the samples in Ferguson et al. (2005), area C shows the highest Li values (Figure GS2017-16-02). Based on the regional groundwater flow for this region (from east to west), the source of Li may be from the weathering of proximal Precambrian rocks underlying the samples sites or from the eastern highlands, which have known hard-rock Li occurrences, such as the Cat Lake–Winnipeg River pegmatite field (including the highly Li-enriched Tanco pegmatite; Černý et al., 1981) and the pegmatites of the Falcon Lake–West Hawk Lake area (Bannatyne, 1985). It is uncertain if the overlying carbonate-rock aquifer would present similar Li ranges, but it nevertheless warrants testing. In the northern extension of the aquifers, Li occurrences in the Wekusko Lake pegmatite field (Černý et al., 1981; Martins et al., GS2017-5, this volume) and Cross Lake pegmatite swarm (Bannatyne, 1985) may also provide a suitable source for enrichment.

Future work

In the next phase of the project, brine samples from existing oil-well operations, as well as from the saline springs, will be collected to analyze them for a range of trace elements and evaluate their mineral potential.

Economic considerations

Saltwater production and disposal from oil wells is a constant issue for the petroleum industry and is one of the dominant reasons for marginal well abandonment. The mineral potential of these brines may serve as an excellent economic opportunity for the operators to improve their profits and extend the life of marginal oil wells, taking advantage of the array of infrastructure already in place for these operations.

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