

Geochemical and isotopic characterization of a regional bedrock/surficial aquifer system, Southeastern Manitoba

Graham Phipps

Manitoba Water Stewardship, Winnipeg, MB, Canada

R.N. Betcher and J. Wang

Manitoba Water Stewardship, Winnipeg, MB, Canada



ABSTRACT

Ordovician-age carbonate and sandstone aquifers form major sources of groundwater supply throughout much of southeastern Manitoba. Recharge to the aquifers is associated with a series of moraines which impose a high head on the eastern sub-crop edge of the bedrock units. Groundwater flow is to the west and northwest with natural discharge from the carbonate unit occurring to the Red River, the Winnipeg Floodway and perhaps to other streams and creeks. Discharge from the highly confined sandstone aquifer is likely by slow seepage through the upper confining layer near or beneath Lake Winnipeg.

As part of a study to evaluate the long-term water supply capacity of the bedrock aquifers in south-eastern Manitoba, an extensive observation well network has recently been installed to supplement existing monitoring points established over the past 40 years. This monitoring network was installed along three flow lines extending from the eastern recharge areas to the western discharge areas. Water sampling and analysis for a broad suite of inorganic and isotopic parameters has been undertaken to characterize the geochemical development and residence times of groundwaters along these flow lines. This information will be used to support the development of a mathematical model of groundwater movement in the area.

RÉSUMÉ

Deux aquifères de l'Ordovicien, l'un carbonaté et l'autre gréseux, constituent des sources importantes d'approvisionnement en eau souterraine dans une grande partie du sud-est du Manitoba. L'apport d'eau aux aquifères est associé à une série de moraines qui causent l'élévation du niveau de l'eau le long de la bordure est subaffleurante du substratum rocheux. L'écoulement souterrain se fait vers l'ouest et le nord-ouest avec un écoulement naturel en provenance de l'aquifère carbonaté dans la rivière Rouge, dans le canal de dérivation de Winnipeg et peut-être dans certains ruisseaux. L'écoulement provenant de l'aquifère gréseux à nappe captive se fait probablement par suintement lent à travers les couches supérieures imperméables situées près du lac Winnipeg ou sous celui-ci.

Dans le cadre d'une étude servant à évaluer la capacité d'approvisionnement en eau à long terme des aquifères du substratum rocheux dans le sud-est du Manitoba, on a créé récemment un réseau étendu de puits d'observation pour compléter les points de surveillance établis au cours des 40 dernières années. Ce réseau de surveillance a été installé le long de trois circuits d'écoulement qui s'étendent des endroits d'apport d'eau à l'est aux endroits d'écoulement à l'ouest. L'échantillonnage et l'analyse de l'eau, visant à déterminer une large gamme de paramètres inorganiques et isotopiques, ont été entrepris afin de découvrir les caractéristiques du développement géochimique et du temps de séjour des eaux souterraines le long de ces circuits d'écoulement. Les données obtenues appuieront le développement d'un modèle mathématique de la circulation des eaux souterraines dans la région.

1 INTRODUCTION

Southeastern Manitoba relies almost exclusively on groundwater for municipal, agricultural, industrial and domestic water source. Major population centres in the area using groundwater include Winnipeg (primarily heating/cooling and industrial use) and Steinbach; the locations of major groundwater withdrawals are shown in Wang et. al., 2008 (these proceedings). Estimates of sustainable pumping have historically been assessed on a project by project basis. However, increasing demands for water due to population pressures, especially close to the city of Winnipeg, rural agricultural expansion and demand for piped water in areas lacking adequate water resources has lead to the need for a more rigorous assessment of the groundwater resources in this area of the province in a regional and systematic manner.

The geochemical study of the groundwater is a component of the overall analysis of these resources which also includes the detailed physical study and the

development of a numerical model (Wang, et. al., 2008) to describe these systems. The geochemical study of these waters is important in developing an overall understanding of these systems and will be used in gaining insight into the processes that impact on water quality as well as those that affect age dating assessment. Residence time assessments will be used to support the numerical model; all of which are important steps in evaluating the sustainability of development of these resources.

2 LOCATION

The study area consists of a large portion of south-eastern Manitoba bounded by the Red River on the west, the Winnipeg River on the north, the international boundary on the south and by pre-Cambrian rocks on the east (Figure 1). The elevation ranges from 217± m (lake Winnipeg) in the north to the regional topographic high of approximately 400 m in the Sandilands in the south-east.

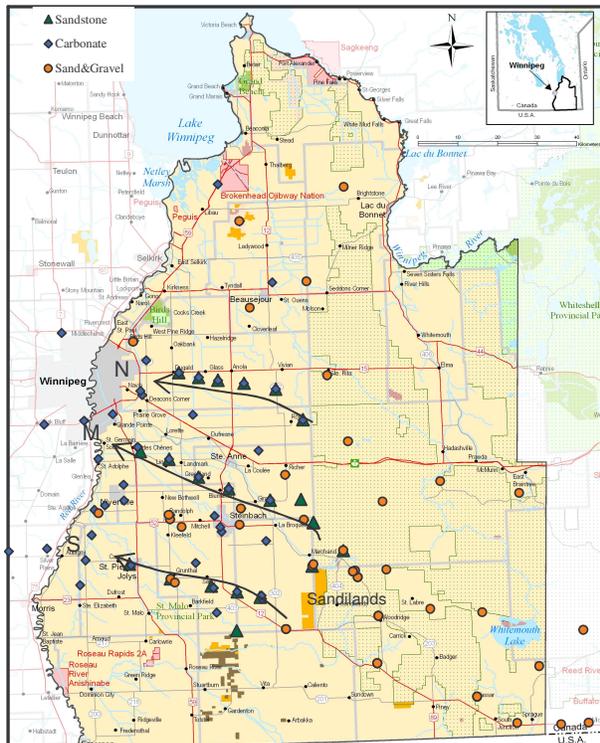


Figure 1. Plan view of the southeastern Manitoba study area and location of sampled wells by aquifer type. Arrows indicate nested wells in the bedrock for the north (N), middle (M) and south (S) flow-lines.

3 GEOLOGY AND REGIONAL HYDROGEOLOGY

The lowest bedrock unit consist of pre-Cambrian metamorphic and granitic rocks of the Canadian Shield which outcrop in the extreme east of the study area but are generally covered by thin Quaternary or Recent sediments. The pre-Cambrian rocks are not included in this study.

Overlying the pre-Cambrian is the Ordovician age Winnipeg Formation consisting primarily of poorly lithified silica sand and shale units (Davis et al., 1962). The Winnipeg Formation averages ~30 m thick. Most hydraulic conductivities obtained from pumping tests on of the sandstone range between 10^{-4} and 10^{-6} ms^{-1} (Betcher et al., 1995, Wang et al., 2008). The sandstone is confined and is isolated from the overlying carbonates by a thin shale layer (Betcher et al., 1995). Differences between the natural piezometric surface and water quality between the sandstone and carbonate provide evidence of this hydraulic separation.

Conformably overlying the Winnipeg Formation are Ordovician age carbonate rocks of the Red River Formation. The Red River Formation consists of dolomitic limestone with argillaceous units (Davis et al., 1962). The thickness of the Red River Formation in the Winnipeg area is approximately 90 m and it thins towards the east due to erosion. Hydraulic conductivity is greatest near the upper surface of the carbonate where permeability through bedding planes, joints, fractures and solution

channels is enhanced. Groundwater yields will vary widely depending on the intersection of drill holes with permeable features. Most hydraulic conductivity measurements vary between 10^{-5} and 10^{-3} ms^{-1} (Wang, et al., 2008).

Except in the extreme south, where Jurassic shales containing evaporites are present, the carbonate aquifer sub-crops throughout most of the region (Figure 7). The location of the erosional edge of the carbonate is shown in Figure 7. Where the overlying carbonate has been eroded the sandstone forms a narrow sub-crop of bedrock. The bedrock units dip gently to the south-west (Figure 2).

Recharge to the regional aquifers is associated with a series of moraines which impose a high head on the eastern sub-crop edge of the bedrock units. Groundwater flow is to the west and northwest with natural discharge from the carbonate unit occurring to the Red River, the Winnipeg Floodway and perhaps to other streams and creeks. Discharge from the highly confined sandstone aquifer is likely by slow seepage through the upper confining layer near or beneath Lake Winnipeg

Surficial and confined sand and gravel aquifers are present in the Sandiland uplands, overlying pre-Cambrian rocks, near the erosional margin of the Ordovician, within glacial tills and sporadically on the lacustrine plain.

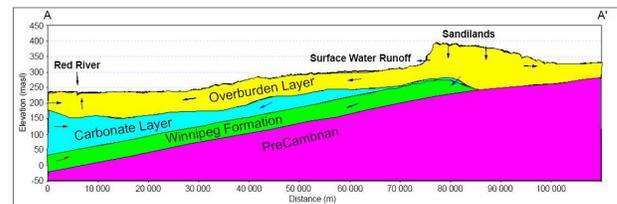


Figure 2. Schematic section of geology from the Red River to the recharge area in southern Manitoba. The overburden layer consists predominantly of lacustrine clay over till in Red River Valley; sand, silt and till in Sandilands uplands, and till with sand units located in between (after Wang, 2008).

4 MONITORING SITES AND DATA COLLECTON

Groundwater samples were collected from wells installed specifically for monitoring groundwater conditions. The monitoring well network consists of wells first installed during the early 1960's up to the present. In 2007 additional wells were completed in the bedrock units along flow lines determined from the existing monitoring network (Figure 1).

Chemical and isotopic samples were collected after thorough well purging, either at the end of a pumping test or after thorough development of the well. Samples were collected following a protocol in which groundwater was lifted by a variable rate submersible pump and within a closed sampling system filtered through a high-volume disposable in-line chemically inert filter ($0.45 \mu\text{m}$). Samples were preserved as necessary on site. Field parameters included temperature, pH, D.O., redox and conductivity and were measured in a flow cell through a bypass line at the time of sampling.

Samples for chemistry were stored on ice and received daily at the laboratory. Isotope samples were

collected following standard sampling and preservation protocols and analysed at the Environment Isotope Laboratory at the University of Waterloo.

5 QUATERNARY AQUIFERS CHEMISTRY

5.1 Sampling Sites

Bedrock carbonate and sandstone units do not crop-out in the study area and are covered by a variable thickness of overburden sediments. Except where the carbonate aquifer is very near surface and karst features have developed, such as in some of the north-central areas of the study region, recharge to these aquifers is through Quaternary sediments. In total, 39 sand and gravel wells were sampled and tested for chemistry, stable isotopes of water and tritium.

Most monitoring wells in sand and gravel aquifers are completed with short, 1.5 m, screens. Target depths vary considerably, from less than 10 metres to almost 90 metres deep. Well locations are shown in Figure 1.

5.2 Major Element Results

Groundwater from sand and gravel aquifers has near neutral pH with relatively low total dissolved solids (TDS) (median = 264 mgL⁻¹). The major element facies is Ca-Mg- HCO₃ (Figure 3). Median calcium and magnesium values are 62.5 and 21.4 mgL⁻¹, respectively. Sodium makes up less than approximately 15% of the total cation milli-equivalents and the median sodium concentration is 7.0 mgL⁻¹. For most sand and gravel waters, bicarbonate constitutes nearly the total anion concentration. The median bicarbonate value is 291 mgL⁻¹ and ranges from 200 to 661 mgL⁻¹. Sulphate concentrations are less than detection in almost 25% of the samples and range to a maximum of approximately 100 mgL⁻¹ with a median concentration of less than 5 mgL⁻¹.

Dissolved oxygen and platinum electrode redox were measured in a limited number of samples (n=9). The dissolved oxygen ranged from 0.02 (oxygen is absent) to 8.3 mgL⁻¹ (near saturation) with a median value of 0.10 mgL⁻¹. All but three samples have D.O. below 0.2 mgL⁻¹; these three wells are less than 25 m deep, although there is not a good relationship between well depth and the presence of oxygen. Redox in these same waters ranged from -20 to +170 mV. Redox values decrease with increasing well depth.

5.3 Conservative Parameters Results

Chloride was detectable in all samples, generally in very low concentrations (median = 1.6 mgL⁻¹). Increased chloride concentration tends to correspond to sites with elevated sodium.

The stable isotopes of water sampled from sand and gravel aquifers are tightly clustered around the average values; $\delta^{18}\text{O}$, -13.3 ± 1.2 and $\delta^2\text{H}$, -100 ± 8.2 (1 σ). Three samples plot enriched and below the general trend, indicative of evaporation prior to infiltration. Removing these three samples results in a local meteoric water line derived from sand and gravel aquifers of $\delta^2\text{H} = 7.6 \cdot \delta^{18}\text{O} + 2.2$, which is almost identical to LMWL

for Gimli MB using global precipitation data (IAEA, 2006). The local meteoric water line and individual samples are plotted in Figure 4.

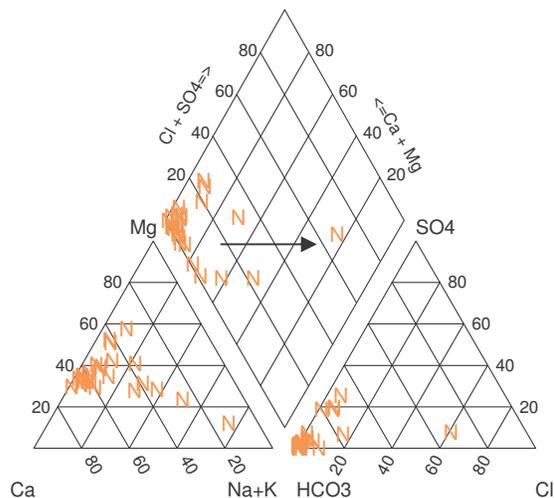


Figure 3. Piper plot of samples from sand & gravel aquifers. The arrow indicates the direction sand and gravel plot when mixing with discharging brackish carbonate water in down gradient locations.

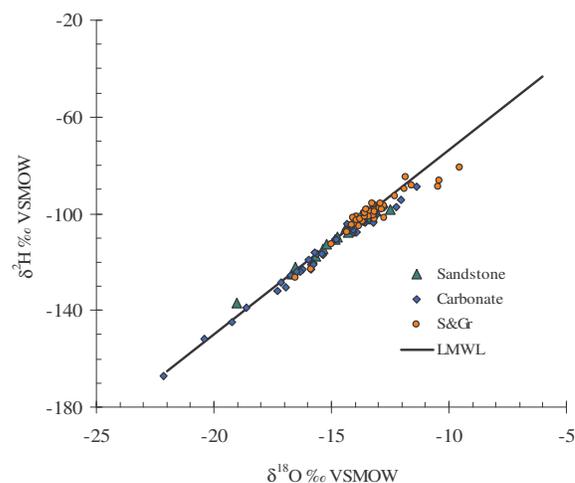


Figure 4. Stable isotopes of water for southeast Manitoba plotted by aquifer type with the local meteoric water line (LMWL) derived from samples from sand & gravel aquifers.

5.4 Tritium

Tritium at the water table of a shallow unconfined sand and gravel aquifer in south-eastern Manitoba is 9.7 ± 1.4 T.U. (unpublished data) which would reflect values in modern recharge. Tritium from sand and gravel aquifers as part of this study are relatively low, ranging from less than detection <0.8 T.U. to 20.4 T.U. Twenty-one samples do not have measurable tritium using the enriched method. Although tritium is below detection in

both shallow and deeper wells, tritium only reaches values of 2 or greater in wells shallower than 40 m.

6 CARBONATE AQUIFER CHEMISTRY

6.1 Sampling Sites

The locations of the sampling sites from the carbonate aquifer are shown in Figure 1. The typical carbonate aquifer well completion consists of casing set into the top of competent rock and the remaining hole in the rock left open. Well depths range from 16.8 to 86.8 m below ground with open portions ranging from 0.8 to 55 m in length, with a median open hole length of 8.9 m. Because of the open-hole completion, water sampled within these wells will represent a mix of groundwater intersected weighted by the hydraulic conductivity of the permeable features encountered. Typically holes ended when great enough permeability had been encountered to complete an adequate water level monitoring site.

6.2 Major Element and Redox Chemistry Results

The total dissolved solids from the carbonate aquifer within the study area ranges from 290 to 5970 mgL⁻¹. Figure 5 shows spatial distribution of dissolved solids superimposed on a map of the heads within the aquifer. Dissolved solids on the eastern extent of the aquifer, near the erosional edge of the carbonate, are in the mid 300 to 400 mgL⁻¹ range and increase systematically down-gradient to >1,000 mgL⁻¹. West of the Red River and south of Winnipeg high salinities up to 18,200 mgL⁻¹ are present. The influence of the saline water can be seen in the southern most sites east of the Red River where the saline / fresh-water boundary lies east of the river. Winnipeg is located approximately at the convergence of three flow systems; a basinal saline water from the southwest with two 'fresh' regional flow systems, one recharged to the northwest of Winnipeg and the 'fresh' waters within the current study area (Fritz et al., 1975).

Calcium concentration ranges from 13 to 331 mgL⁻¹, with 75% of the samples containing less than 80 mgL⁻¹. The median calcium is 66.5 mgL⁻¹. Magnesium ranges from 7.3 to 216 mgL⁻¹; with a median concentration of 37.3 mgL⁻¹. Sodium ranges from 4.3 to 2070 mgL⁻¹ with a median concentration of 45.8 mgL⁻¹. At concentrations above approximately 80 mgL⁻¹ the molar ratio of Na and Cl is ~1 (Figure 11).

In all but approximately 10% of the samples, those that are the most mineralized, bicarbonate is the dominant anion. The median bicarbonate concentration is 383 mgL⁻¹ and ranges from 261 to 681 mgL⁻¹. Sulphate varies from less than detection in almost 25% of the samples to a maximum of approximately 1010 mgL⁻¹ with a median concentration of less than 38.6 mgL⁻¹.

Measured pH ranges from 7.0 to 8.1, with a median value of 7.5. Redox and D.O. were measured in 17 sites. The D.O. ranges from 0.03 (oxygen is absent) to 1.14 mgL⁻¹. Only one sample has greater than 1 mgL⁻¹, whereas the remaining samples are almost completely depleted of oxygen, containing less than 0.20 mgL⁻¹. Eh ranges from -223 to 244 mV.

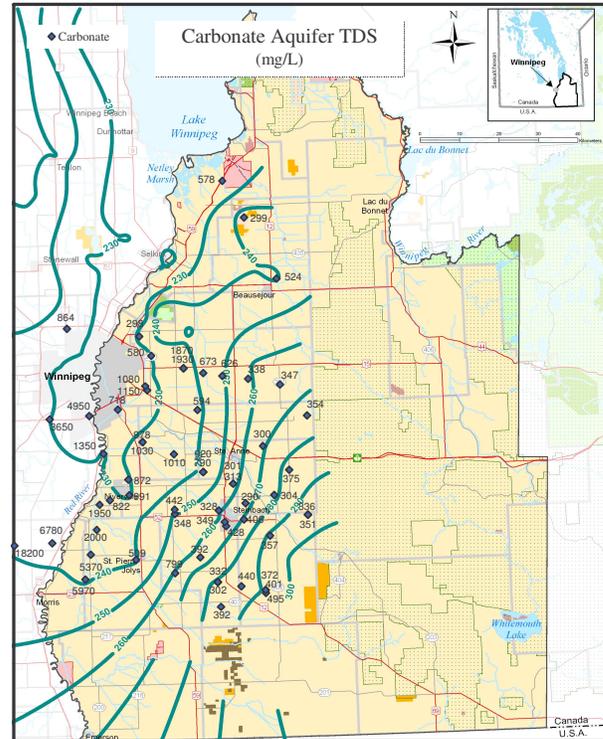


Figure 5. Contour of the piezometric surface from the carbonate rock aquifer (m asl). Sampling locations (blue diamonds) are labelled with TDS concentrations (mgL⁻¹). TDS from carbonate wells outside the study area are plotted for reference.

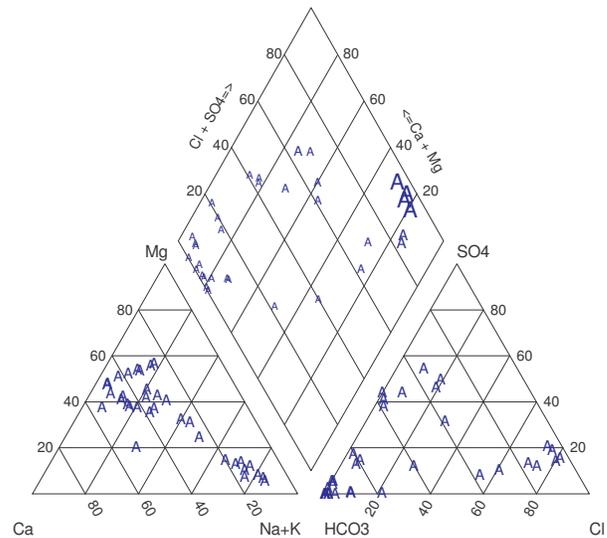


Figure 6. Piper plot of carbonate water. Symbol size in the diamond is proportional to TDS.

6.3 Conservative Element Results

Chloride concentrations in samples from the carbonate aquifer range from 0.5 to 2950 mgL⁻¹ (Figure 7). Low concentrations of chloride (<5 mgL⁻¹) are present in most of the eastern half of the aquifer. The northern most

portion of the aquifer typically contains the lowest chloride and the entire northern flow-line contains $\sim <20 \text{ mgL}^{-1}$. Along the middle and southern flow-lines, chloride increases downgradient to values approximately 100 mgL^{-1} before there is a sharp increase to values $>2000 \text{ mgL}^{-1}$ (Figure 7), in the area south of Winnipeg. There is a very good linear relationship between chloride and TDS, especially in waters with chloride concentrations greater than approximately 100 mgL^{-1} .

The average value of stable isotopes of water from the carbonate aquifers is $\delta^{18}\text{O}$, -13.3 ± 1.2 and $\delta^2\text{H}$, -100 ± 8.2 ($\pm 1\sigma$). The distribution as compared to the global meteoric water line is shown in Figure 4. Strongly depleted isotopes of water are indicative of recharge during a colder Pleistocene climate. The four highly depleted samples from the carbonate aquifer ($\delta^{18}\text{O} < -18\text{‰}$) are all located west of the Red River where glacial water has mixed with saline basin water (Render and Fritz, 1975; Grasby and Betcher, 2002).

The relationship between $\delta^{18}\text{O}$ and chloride shows there is a very distinct relationship between these two conservative parameters (Figure 8). Waters with elevated chloride are all associated with depleted $\delta^{18}\text{O}$; whereas low chloride concentrations ($\sim <2 \text{ mmol}$) are associated with post-glacial water.

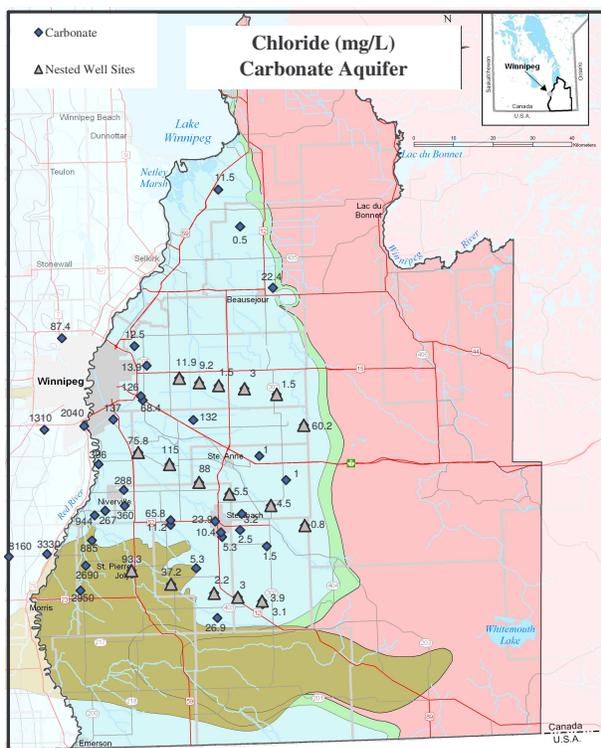


Figure 7. Chloride (mgL^{-1}) in water from the carbonate aquifer. Grey triangle represent well nest locations for 3 flow-lines. The bedrock geology on this map is shown as pre-Cambrian (pink shading), sandstone sub-crop (green band), carbonate sub-crop (blue) and the Jurassic-age formations (brown).

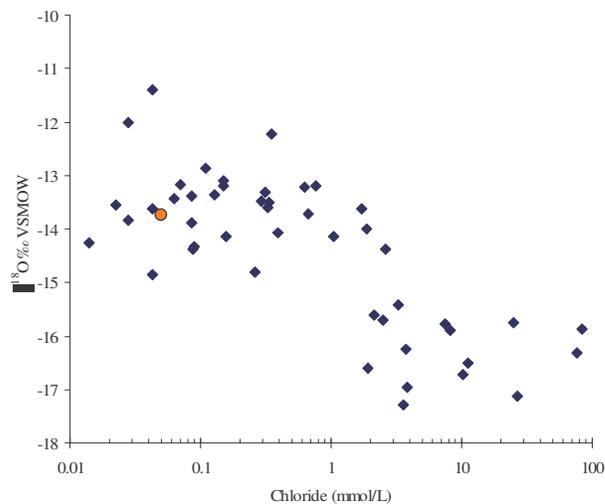


Figure 8. Plot of $\delta^{18}\text{O}$ and chloride from the carbonate aquifer within the study area (blue diamonds). Average value from the sand and gravel aquifers ($n=9$) near the erosional edge is shown (orange circle).

7 SANDSTONE AQUIFER CHEMISTRY

7.1 Sampling Sites

Wells in the Winnipeg Formation sandstone range in depth from 41 to 133 m and consist of a short, 0.6 to 4 m length, screen completion. The median well depth is 87 m. Because of formation collapse during drilling, screens were generally set in the uppermost part of the aquifer. The locations of the sampling sites are shown in Figure 9.

7.2 Major Element Chemistry Results

The overall TDS of water from the sandstone is relatively low, ranging from 189 to 1320 mgL^{-1} with a median value of 325 mgL^{-1} . The TDS is in the 200 to 300 mgL^{-1} range near the sandstone subcrop (Figure 9). TDS increases very gradually along the flow direction to values in the 300 to 400 mgL^{-1} range. Only in the final sample along each flow-line does the TDS increase to above 500 mgL^{-1} . The exception to the observation of low TDS in the subcrop region is shown in the southernmost sampled well which has the highest TDS of wells sampled. This sample has high concentrations of calcium and sulphate, low chloride and plots distinct from the other sandstone water (Figure 10). The most plausible explanation for the anomalous chemistry is that gypsum is reported within the upper confining shale unit in the log from this well.

Bicarbonate ranges from 226 to 532 mgL^{-1} with a median concentration of 346 mgL^{-1} and is the dominant anion in the low mineralized waters ($\text{TDS} < 500 \text{ mgL}^{-1}$). Sulphate concentrations are quite low within the sandstone aquifer. Groundwater near the sandstone erosional edge has sulphate concentrations generally $<3 \text{ mgL}^{-1}$ which frequently decreases to below detection values down-gradient. Sulphate concentration and percent content increase in the highest TDS water.

Calcium and magnesium concentrations range from 6.7 to 189 mgL⁻¹, and 1.9 to 50, with median values of 32 and 18 mgL⁻¹, respectively. Median hardness of the water is 141 mgL⁻¹ as CaCO₃, and 25% of the samples are below 100 mgL⁻¹. The relatively low TDS and low hardness are properties that make the sandstone aquifer a desirable domestic water source. Along the middle and northern flow-lines calcium and magnesium concentrations approximately double from the recharge values and then decrease along the flow path to concentrations ~<20 mgL⁻¹, and <10 mgL⁻¹, respectively.

Sodium values range from 18 to 376 mgL⁻¹. Median Na is 65 mgL⁻¹. At higher concentration sodium, and potassium, constitute >80 percent of the cation meq (Figure 10).

pH varies from 7.2 to 8.2 (median = 7.6). Only one sample, located near the erosional margin, had D.O. concentration > 1 mgL⁻¹ and three other samples had low concentrations >0.1 mgL⁻¹, however, the remainder had concentrations of 0.06 and lower (effectively 0 mgL⁻¹ D.O.) (n = 18). The Eh ranges from -30 to +181 mV.

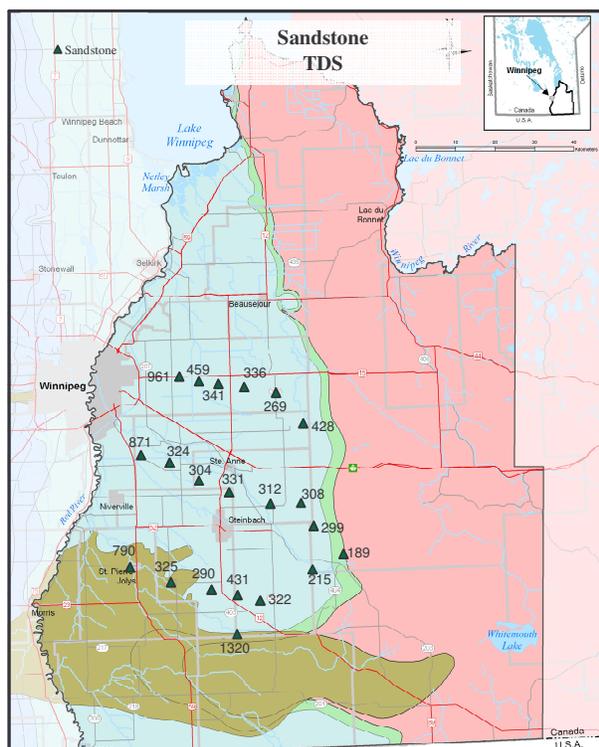


Figure 9. Location of Winnipeg Formation Sandstone wells and total dissolved solids from each site.

7.3 Conservative Elements

Chloride systematically increases down-gradient in magnitude and proportion of anions. Near the sandstone subcrop chloride concentration in the northern flow line are generally <20 mgL⁻¹, and in the middle and southern flow lines <5 mgL⁻¹. Chloride increases to values <40 mgL⁻¹ along the generalized flow direction and is around or greater than 300 mgL⁻¹ in the last well in each of the three flow lines.

Stable isotopes vary from -19.0 to -13.1‰ for δ¹⁸O and -137 to -98.9‰ for δ²H. In upgradient positions the chloride - δ¹⁸O are similar to sand & gravel aquifer values whereas the most depleted values correspond to increased chloride which occurs in the downgradient locations.

8 MAJOR ELEMENT GEOCHEMICAL EVOLUTION

8.1 Sand & Gravel Aquifers and Recharge Chemistry

The dominant ion chemistry in the topographic uplands is predominantly Ca-Mg-HCO₃. There is very little change in major element ratios except in down gradient locations, where the carbonate heads are greater than the sand and gravel aquifers and there is discharge from the carbonate aquifers to the overlying Quaternary aquifers. In these cases the waters plot with increasing chloride content (Figure 11) and trend away from the Ca-Mg- HCO₃ apex of the piper diamond on Figure 6.

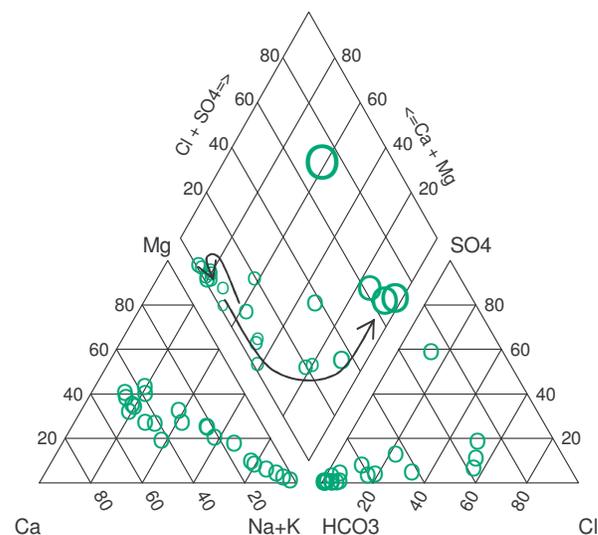


Figure 10. Piper plot of water from sandstone aquifer. Symbol size is proportional to TDS. The arrow indicates the general chemical trend along the flow direction. The single point with a high proportion of sulphate is located near Jurassic-aged rocks containing evaporates.

8.1.1 Carbonate Aquifer

The major ion facies of carbonate water shows a complex geochemical development within the aquifer (Figure 12). The major element facies in the eastern and northern areas is low TDS (Ca, Mg)-HCO₃ recharge type water, similar to overlying sand and gravel aquifers. The concentrations and proportion of sodium and chloride increases along the generalized flow direction and are greatest in the south-western area of the study; at the end of the basin-wide flow of saline water. These plot with the greatest concentrations of sodium and chloride in Figure 11 and represent an end-member of water quality within the study area. At low chloride concentrations most sodium from the carbonate aquifer plots above an ideal mixing curve between sand and gravel recharge quality

water and high TDS carbonate water (Figure 11). As well, most water from the carbonate aquifer plots within the lower half of the piper diamond (Figure 10). These relations indicate a freshening trend of groundwater with cation exchange during freshening. Higher TDS Na-Cl type waters have been displaced by lower TDS bicarbonate type water while exchanging calcium-magnesium with sodium sorbed to aquifer material.

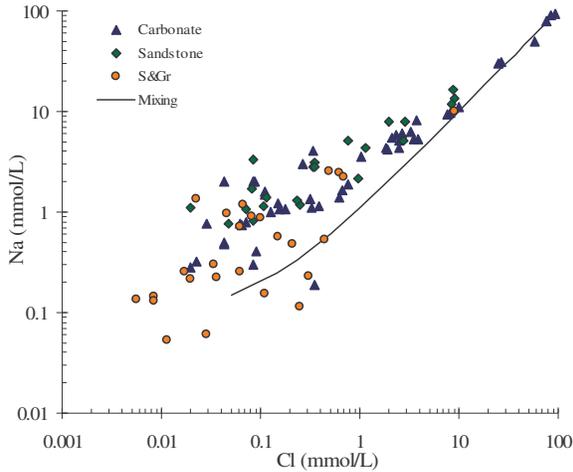


Figure 11. Plot of sodium vs. chloride for all samples. The mixing line denotes an ideal mixing between sand and gravel aquifer water located near the erosional boundary ($n=9$) and the most mineralized water from the carbonate aquifer within the study area.

The low T.D.S. Na-(Mg)- HCO_3 -Cl water that truncates the otherwise typical (Ca, Mg)- HCO_3 recharge type water in the central eastern area is inconsistent with these observations. One possibility of its occurrence could be from cross-contamination (open drill holes) with the underlying sandstone aquifer. The nested sandstone monitoring well (the carbonate and sandstone wells are completed into separate drill holes) on the eastern side of this anomaly has Na- HCO_3 -Cl type water. The chloride in this sandstone well is greater ($\text{Cl} \sim 100 \text{ mgL}^{-1}$) than sandstone wells further along the defined flow line. Chemistry from private wells completed in the carbonate throughout this area shows that elevated chloride (80 to 100 mgL^{-1}) is common in many of the well waters. The reason why there is higher chloride than expected in an up-gradient area in both aquifers requires further study. The relationship between chloride and $\delta^{18}\text{O}$ (Figure 8) implies flushing of the residual mixture of Pleistocene and basin-derived water by post-glacial water follows a piston flow model and the residual chloride in this part of the aquifer indicates that post-glacial recharge has been somewhat restricted in this area.

There is not a good relationship between sulphate and chloride although high sulphate, up to 1000 mgL^{-1} is associated with the high TDS water at the end of the defined flow paths. An increase in the proportion of sulphate is most prevalent in the central portion of the study area. Although gypsum or anhydrite is reported above carbonate rock from drill logs in Jurassic aged

rocks; these occurrences are south of the observed sulphate type water and therefore wouldn't contribute to these observations. In the central portion of the study area the source of the sulphate, either from the formation, residual high TDS water or leakage from overlying Quaternary sediments (tills and clays) requires additional investigation.

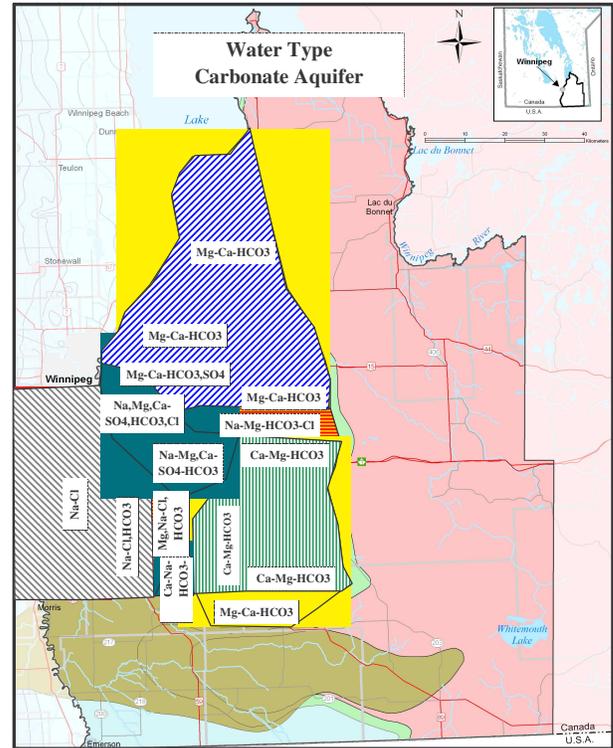


Figure 12. Distribution of major water types within the carbonate aquifer.

8.1.2 Sandstone Aquifer

In the Winnipeg sandstone aquifer the major ion chemistry along the northern flow-line evolves from Na-Mg-Ca- HCO_3 to Na- HCO_3 to Na-Cl- HCO_3 type water. A similar evolution is seen in the middle and southern flow lines (Figure 10) except sodium is less prevalent in the initial water. The freshening of the aquifer is shown as the Na-Cl water is displaced by low chloride water and cation exchange takes place resulting in naturally softened water.

There is a reasonably good relationship between measured sulphate and chloride concentrations (Figure 13) from the sandstone aquifer. Both of these analytes have very low concentrations in the recharge water and upgradient positions and increase along the flow path with maximum concentrations closest to the fresh / saline water boundary near the Red River.

The relationship between chloride, originating from residual saline water within the aquifer, and $\delta^{18}\text{O}_{\text{water}}$ give some indication of the elution process during aquifer freshening. The northern most flow-line contains a greater proportion of depleted $\delta^{18}\text{O}$ along the flow path and the proportion of post glacial water is greater in the middle

and southern flow-lines (Figure 14). The greater proportion of post-glacial water corresponds to flow-lines with less sodium in the up-gradient area indicating a greater amount of flushing in these areas.

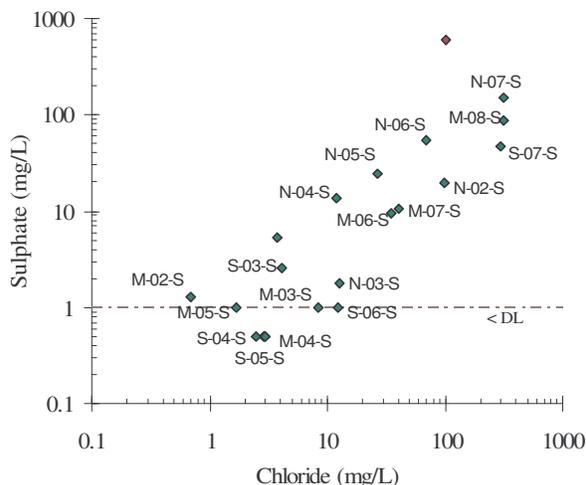


Figure 13. Relationship between chloride and sulphate in water from the sandstone aquifer. Sites from the 3 flow lines are labeled (i.e. M-05-S: M = middle flow line, 5 = relative position along flow line, S = sandstone). The point labeled in red is the high TDS water from the most southern site (see Figure 9).

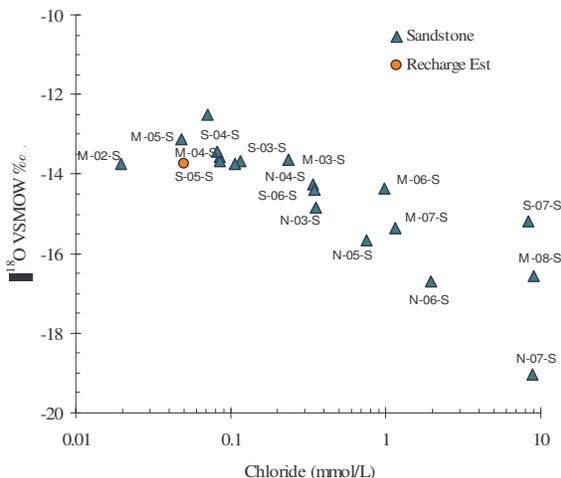


Figure 14. Relationship between chloride and ¹⁸O in water from the sandstone aquifer. Sites follow a similar labeling as in Figure 13. Average value from the sand and gravel aquifers near the erosional edge is shown for comparison (n=9).

9 SUMMARY

The chemistry in the bedrock aquifers, especially the Carbonate aquifer, shows a complex development from the primary recharge areas located near the Sandilands upland and along the erosional margin of the bedrock to

downgradient locations. High concentrations of major ions within both the carbonate and sandstone aquifers, except for sulphate within the carbonate aquifer, are related to mix of glacial (depleted δ¹⁸O) and residual Na-Cl saline water. In both the sandstone and the carbonate aquifers post-glacial Ca-Mg-HCO₃ water is actively flushing this mix through the aquifers. This results in aquifer 'freshening' taking place throughout most areas of the bedrock aquifers east of the salt water boundary and natural water softening in large portions of the sandstone. Post-glacial waters are associated with very low concentrations of chloride however the advance of 'fresh' water is not uniform throughout the aquifers. In the sandstone aquifer a greater proportion of post-glacial recharge is seen further along the flow-path in the south as compared to the north; whereas a greater degree of chloride elution has occurred along the northern flow-line in the carbonate as compared to the south.

The recent addition of monitoring wells along defined flow-paths will enable further understanding of the groundwater geochemical development; especially in the sandstone aquifer where few wells were previously dedicated to monitoring the aquifer.

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