GEOLOGICAL SURVEY OF CANADA
OPEN FILE 7449

A Study of Groundwater Quality from Domestic Wells in the Sussex and Elgin Regions, New Brunswick: with Comparison to Deep Formation Water and Gas from the McCully Gas Field

T.A. Al, J. Leblanc and S. Phillips

2013

Natural Resources Canada
Ressources naturelles Canada

GEOLOGICAL SURVEY OF CANADA
OPEN FILE 7449

A Study of Groundwater Quality from Domestic Wells in the Sussex and Elgin Regions, New Brunswick: with Comparison to Deep Formation Water and Gas from the McCully Gas Field

T.A. Al, J. Leblanc and S. Phillips

Department of Earth Sciences, University of New Brunswick, Fredericton, NB E3B 5A3

This work was performed for the GSC as part of PERD project "Unconventional gas potential from Paleozoic shales of eastern Canada – addressing knowledge gaps for sustainable development"

2013

doi:10.4095/292762

Recommended citation
Al, T.A., Leblanc, J., and Phillips, S. 2013. A study of Groundwater Quality from Domestic Wells in the Sussex and Elgin Regtion, New Brunswick: with Comparison to Deep Formation Water and Gas from the McCully Gas Field.; Geological Survey of Canada, Open File 7449, 40p. doi:10.4095/292762

TABLE OF CONTENTS

LIST OF APPENDICES

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

The exploration for shale gas in Canada has led to the identification of a huge volume of in-place and marketable natural gas with the potential of supplying clean burning fuel for many decades. However, some controversies exist on the technique used to unlock these new riches; that is hydraulic fracturing from high-pressure injection of slickwater, a mixture of water, chemicals and proppants (sand) in order to create and keep open small fractures in the target shale.

The Carboniferous Frederick Brook shale and the overlying Hiram Brook sandstone in southern New Brunswick are identified as promising sources for shale gas. Preliminary evaluation of in-place resources by one operator in the Moncton sub-basin suggests 67 Tcf of natural gas in their acreage. At the McCully gas field, there is production from one vertical well in the Frederick Brook shale but most of the production is from tight sandstone of the Hiram Brook Member. Initial exploration specific to shale gas has led to high expectations but inconclusive results. In the same period, societal concerns about the risk of groundwater contamination from shale gas exploration activities have increased significantly in New Brunswick. The Geological Survey of Canada, in collaboration with eastern Canada provincial stakeholders has initiated a four-year research project (2011-2015) designed to evaluate the potential of natural connectivity between the deep-seated shales and the shallow groundwater.

In 2012-2013, the Department of Earth Sciences at the University of New Brunswick carried out a sampling program of 26 water wells from the area around the McCully gas field near Sussex; the operator of the McCully gas field provided gas and brine samples for chemical and isotopic comparison. This gas field has experienced multiple hydraulic fracturing events in vertical wells for the development of the tight sandstone gas reservoir from 2000 to 2008.

The research program consisted of field measurements (pH, redox and alkalinity) as well as groundwater sampling for isotope analyses (^{18}O and ^{2}H) and inorganic chemistry, measurements of dissolved hydrocarbons (methane, ethane and propane) and isotope analyses (^{13}C and ^{2}H) of dissolved methane. Methane from the gas field was isotopically characterized as well as the inorganic chemistry of the brine.

The McCully brine has concentrations of Na, Cl and Br that are hundreds of times higher than that of shallow groundwater. Concentrations of K, Ca, Mg and SO_4 are also higher than those of shallow groundwater; from its chemistry, the brine is likely derived from seawater and comparison with shallow groundwater does not indicate mixing.

Gas produced at McCully is methane (91 – 94%) with ethane (2 – 6%) and propane (0.1 – 1%). Isotopic analyses of the methane suggest a thermogenic origin. No ethane or propane was measured in the groundwater and methane was detected in 3 domestic wells. Concentrations are very low (0.01, 0.11 and 1.17 mg/L); the 3 samples are outside the McCully gas field area. Two of these samples had enough methane for

isotopic analyses, one suggestive of a thermogenic origin and the other is enriched in ^{2}H that could be related to oxidation of methane.

1. Introduction

1.1. Unconventional Gas Development

The term unconventional refers to hydrocarbon reservoirs that require stimulation, generally with hydraulic fracturing (fracking), to promote the flow of gas and oil from rocks that have low permeability relative to conventional reservoirs. Over the last decade, unconventional oil and gas development and production have occurred with increasing frequency. For example, in Arkansas, unconventional drilling began in 2004 and by 2011 it was estimated that approximately 4000 wells had been drilled (Kresse et al. 2011). In Canada, unconventional oil and gas production is underway in several provinces, including New Brunswick, and it has become a major contributor to natural resource production in British Columbia (Stefik and Paulson, 2011).

The potential economic and environmental consequences, and the challenges to regulators of unconventional hydrocarbon production have received a great deal of attention internationally (Kargbo et al. 2010). In Canada the regulatory response to this rapid increase in unconventional resource development has been mixed, ranging from a ban on exploration and development activities in Quebec, to provincial support in Alberta and British Columbia.

1.1.1. Gas Development in New Brunswick

New Brunswick is one of the oldest oil-producing provinces in Canada. In 1859, one of the first oil wells in North America was drilled just outside of Moncton, NB, on the east side of the Petitcodiac river near the village of Dover (St. Peter, 2000). Subsequently, additional wells were drilled and produced a small quantity of oil (Hea, 1974). Historic production in the Dover area (known as the Stoney Creek field; Figure 1) was from conventional oil wells that were drilled into the Lower Carboniferous lacustrine sandstones of the Albert Formation. Most oil and gas development in New Brunswick has focused on the Albert Formation of the Moncton subbasin (Figure 1).

Corridor Resources currently produce natural gas at the McCully field near Sussex (Figure 1); production is primarily from the Hiram Brook sandstone (Figure 2), but there is one well in the Frederick Brook shale. These wells are considered unconventional because the Hiram Brook sandstone and the Frederick Brook shale at the McCully field require fracking stimulation to promote economic production.

Recent exploration activities outside the McCully field include a joint project between Corridor Resources and Apache Corp. to test the resource potential near the town of Elgin (Figure 3). Other companies have shown an interest in exploring elsewhere in the Maritimes basin (Figure 4), but at this time production in New Brunswick is limited to the McCully field.

There has been considerable public debate in New Brunswick about the potential environmental impacts from unconventional hydrocarbon exploration and development, with the principal concerns focused on the use of water resources for fracking, and the potential for groundwater contamination from fracking fluids and leaking well casings.

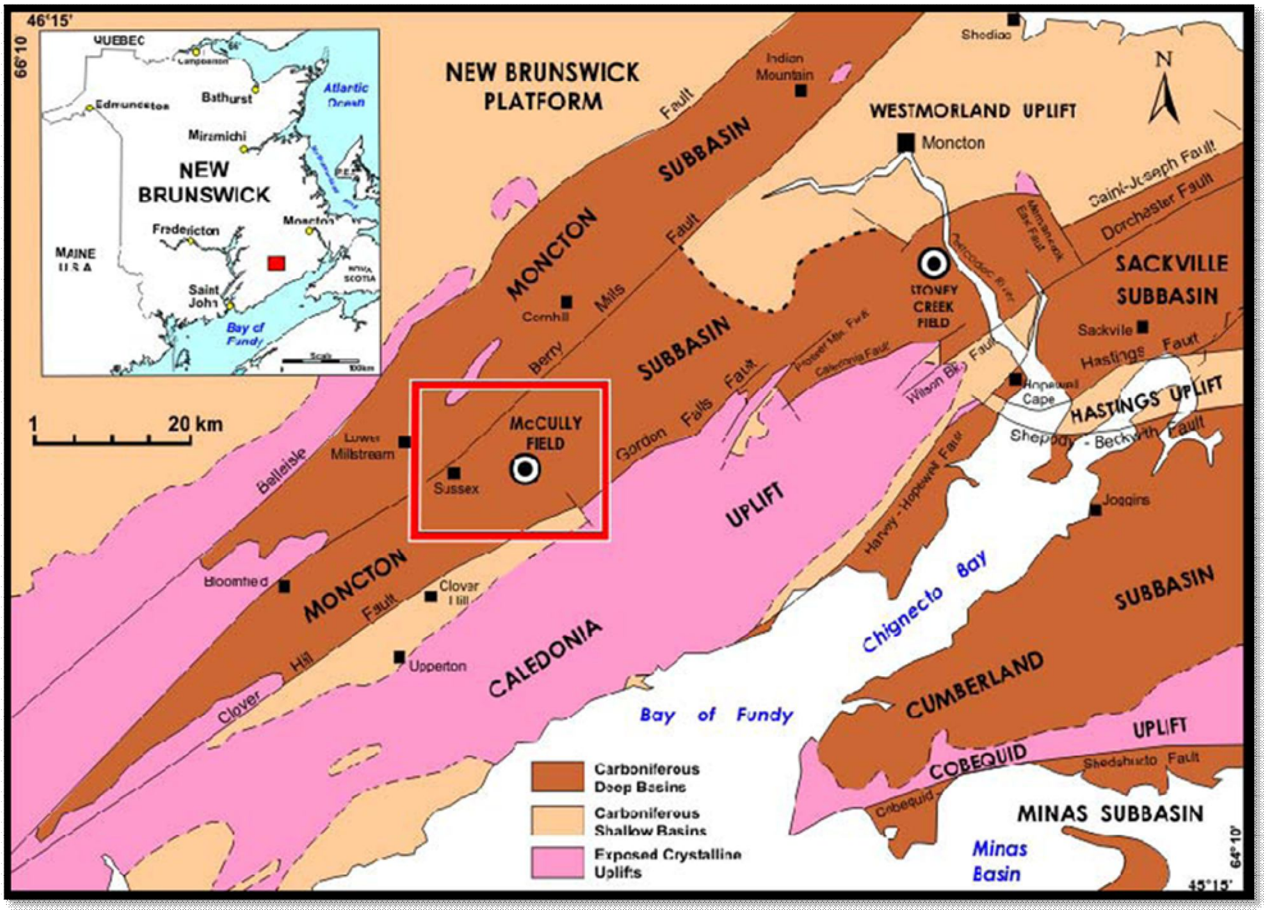

Figure 1. Location of McCully field and the Stoney Creek field in the Moncton subbasin (Hinds and St. Peter, 2005).

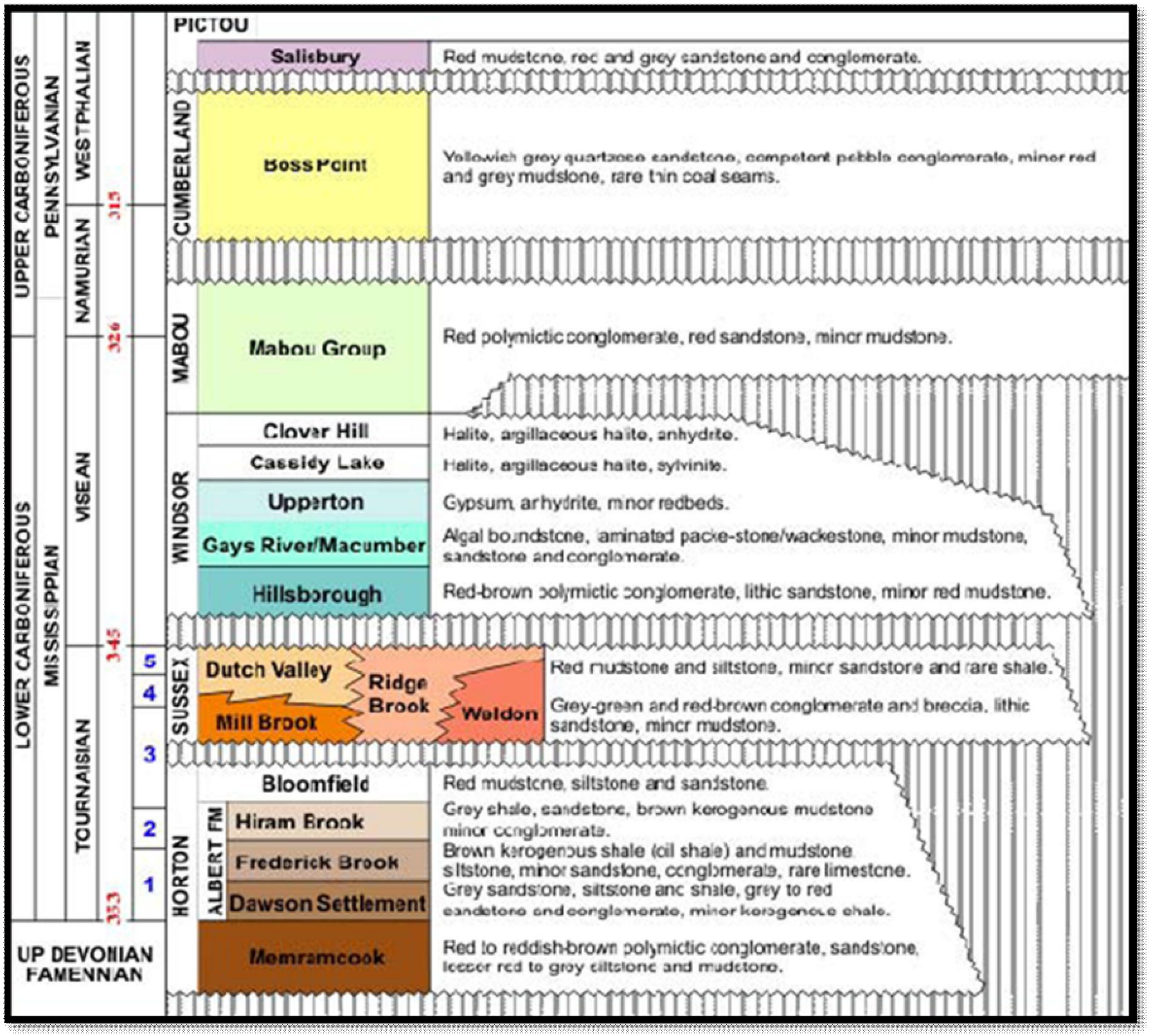

Figure 2. Stratigraphic column for the Carboniferous at the McCully field. Gas production is from the Hiram Brook sandstone and the Frederick Brook shale, which are part of the Albert Formation (Hinds and St. Peter, 2005).

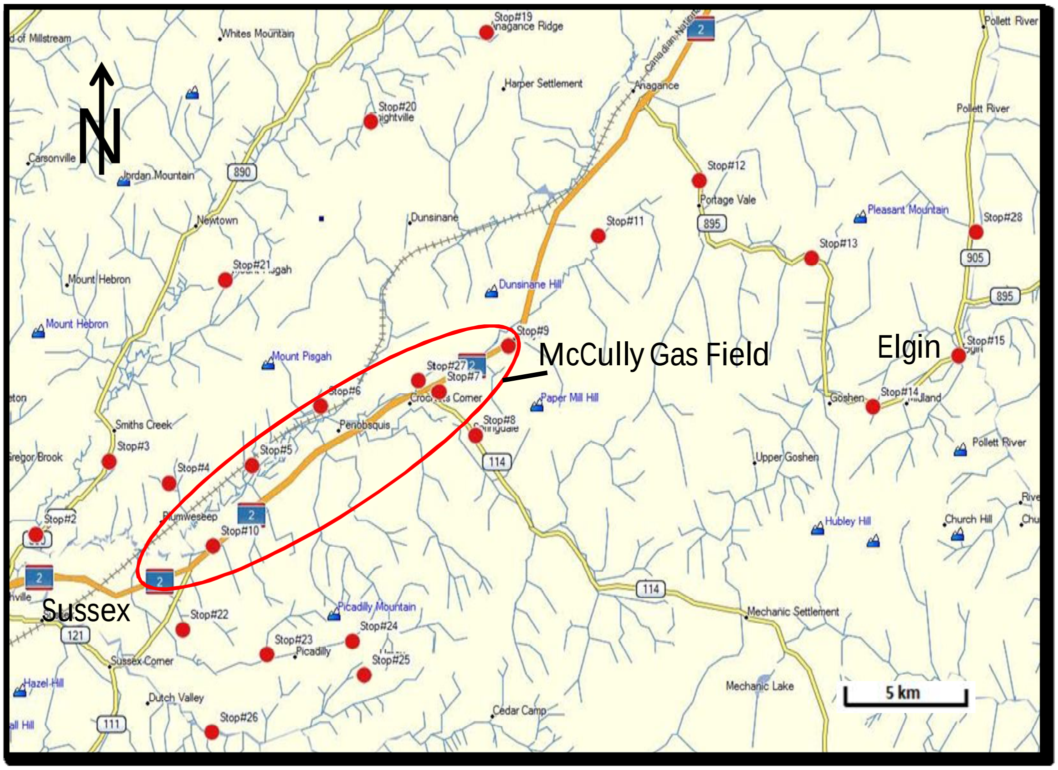

Figure 3. Study area showing the location of the McCully Gas Field and the locations of shallow groundwater samples.

1.2. Objectives

Baseline determination is one of the common approaches to identifying environmental impacts from development activities. This approach may be applied to identify impacts to a variety of environmental components such as air, water, flora and fauna. The Province of New Brunswick has committed to a requirement for baseline testing of surface water and groundwater quality prior to hydrocarbon exploration and development activities. The objective of the present study is to conduct an orientation-style survey of groundwater quality in the Sussex – Elgin region whereby the geochemical characteristics of the deep formation water and gas from the McCully field in New Brunswick will be measured along with the geochemical characteristics of shallow groundwater. The study will contribute to an understanding of the geochemical parameters relevant to baseline water testing efforts that are under consideration by the Government of New Brunswick.

This project is part of and funded by the Geological Survey of Canada, 2011-2015 PERD project on evaluation of the geological integrity of shale gas cap rock in eastern Canada.

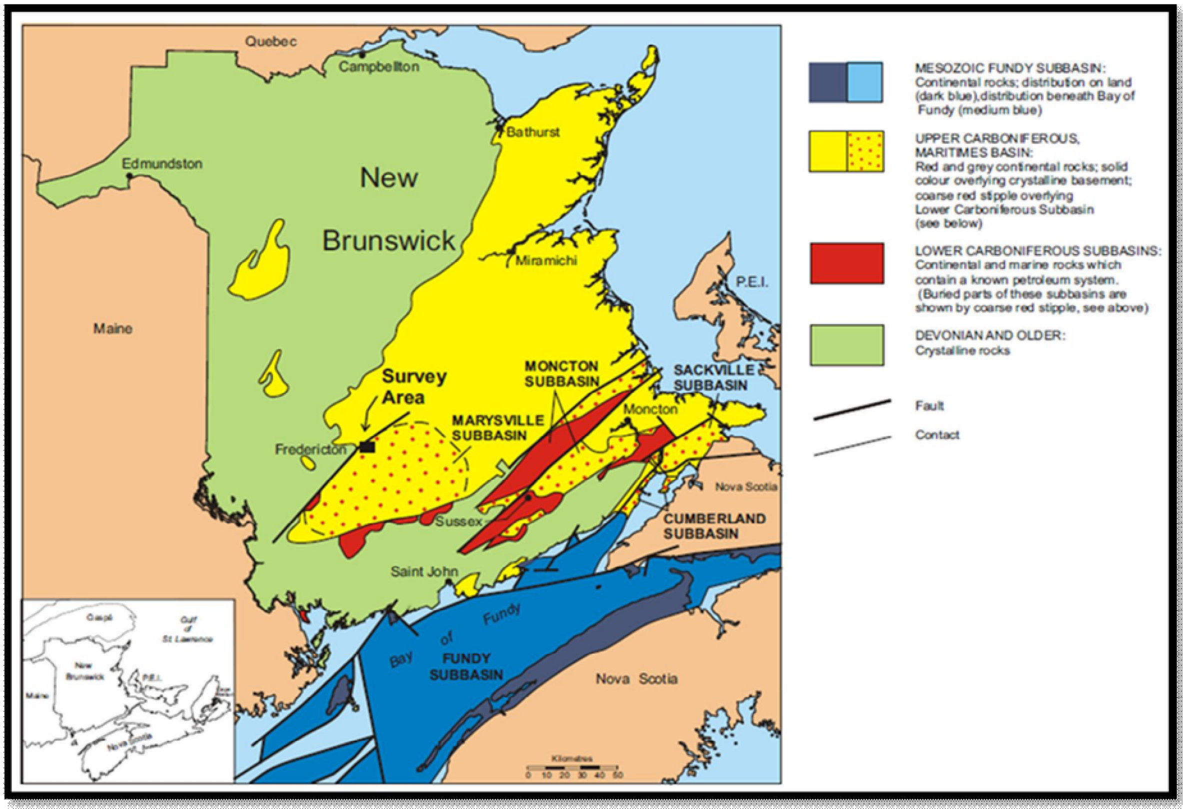

Figure 4. General geology of New Brunswick showing the Carboniferous Maritimes Basin, which includes the Moncton subbasin (St. Peter, 2000).

1.3. Approach

The present study involves sampling and analysis of 26 domestic water wells (Figure 3) from an area around the McCully Gas Field, in addition to sampling and analysis of the deep brine and gas recovered from producing wells in the McCully field. Shallow groundwater and deep brines were analyzed for major ions, trace metals, isotopes (^{18}O and ^{2}H), hydrocarbon content (methane, ethane, and propane) and the isotopic composition (^{13}C and ^{2}H) of methane dissolved in water. The isotopic composition of methane from the McCully field was also determined. The results are intended to aid in defining the range of geochemical characteristics for inorganic aqueous solutes and dissolved methane in shallow groundwater, and provide a basis for comparison with the geochemical characteristics of the brine and methane produced from the McCully reservoir.

Water-supply wells are not ideal for the intended purpose because they are not constructed to provide high-quality geochemical samples that are representative of the geochemical conditions in the aquifer. Water samples collected from supply wells are prone to artifacts from degassing, turbidity, oxidation related to contact with atmospheric O_2 in the well casing, reactions with the well casing and water pipes, and the inability to adequately purge stale water from the well prior to sampling. The alternative is to use piezometers that have been properly constructed for geochemical investigations, but these are rarely available over widespread geographic areas for baseline sampling, and they are not available in this case.

2. Methods

2.1. Shallow Groundwater Sample Collection

Domestic water well samples were always collected from water lines upstream of any water-treatment system. The pump and water-line system was purged for approximately five minutes prior to sample collection.

2.1.1. Field Measurements

Field parameters (pH, redox potential and alkalinity) were measured at each site. The pH and redox potential were measured potentiometrically with a Ross combination electrode (Model 815600) and an Orion platinum redox electrode (Model 98-78-00) respectively. Alkalinity was determined colourimetrically on filtered water samples (0.45 µm) with a Hach digital titrator and standardized 0.16 and 1.6 N H_2SO_4. The pH electrode was calibrated before each measurement and the calibration was checked following the measurement. The redox electrode was checked before and after each measurement using Zobell's solution. All redox values are referenced to the standard hydrogen electrode (E_H).

2.1.2. Water Isotopes

Samples for water isotopes (^{18}O and ^{2}H) were collected without filtration into 20 mL glass scintillation vials. The vials were pre-rinsed with sample water and filled with zero head space. Samples were stored on ice in the field and then refrigerated prior to analysis. Analyses were conducted at the University of Ottawa G.G. Hatch Isotope Lab.

2.1.3. Dissolved Hydrocarbons

Water samples for dissolved hydrocarbon analysis were collected in 500 mL glass Wheaton bottles with butyl rubber seals and aluminum crimp caps. Samples were collected by connecting a tygon tube to the homeowner's tap, inserting the tube to the base of the bottle and allowing overflow for several minutes, then withdrawing the tube and immediately capping while ensuring that there was zero head space. Samples were stored on ice in the field and then in the fridge until analyses.

Analyses were conducted by GC/FID (method AQS90) at the Research and Productivity Council (RPC) labs in Fredericton, New Brunswick. Analytes included methane, ethane and propane, but ethane and propane were not detected. The method detection limit for methane is 0.01 mg/L.

2.1.4. $\delta^{13}C$ and $\delta^{2}H$ Isotopes of Dissolved Methane

Water samples for determination of methane isotopic composition ($\delta^{13}C$ and $\delta^{2}H$) were collected in 500 mL glass Wheaton bottles with butyl rubber seals and aluminum crimp caps. Samples were collected as described above for dissolved hydrocarbons.

Methane isotope analyses were conducted at the University of Ottawa G.G. Hatch Isotope Lab.

2.2. McCully Brine

A small volume of brine flows from the reservoir sandstone to the well head during gas production. In addition, the hydrocarbon gas produced at the well head contains water vapour and this moisture is removed from the gas by absorption in methanol that is injected at the wellhead. The gas – brine – methanol mixture flows to a liquid-gas separator at the production plant where samples of methanol-brine mixture are collected for analysis. Corridor Resources personnel collect samples of the brine on a routine basis for inorganic chemical analyses. These data were provided by Corridor Resources. Samples were collected for water isotope analyses but no data are reported because it was not possible to separate brine from the methanol without causing isotopic fractionation.

2.3. Gas Collection and Analysis

Production gas samples were collected at the well head in stainless steel, flow-through cylinders provided by SGS Canada Inc., Point Tupper, Nova Scotia. Gas was transferred from the cylinders into evacuated 60 mL Wheaton bottles and analysed for $\delta^{13}C$ and $\delta^{2}H$ isotopic composition at the University of Ottawa, G.G. Hatch Isotope Lab by isotope ratio mass spectrometry.

3. Results and Discussion

3.1. McCully Brine

Two types of deep brine samples were collected and analyzed for inorganic chemistry from the McCully Gas Field by Corridor Resources personnel. One sample was collected from the low temperature inlet separator, which is a mixture of produced water, gas, and methanol. The remaining samples (total: 11) were collected down the processing stream, where the water vapour associated with the production gas has been combined with the waste water. A summary of the inorganic chemistry for the deep brine is shown in Table 1. It is important to note that the brine-chemistry data are probably influenced by the water collection and separation processes in the wells and production plant, and likely do not accurately represent the in-situ brine composition.

Table 1 – Summary of the inorganic chemistry of the deep brine. A complete list of results can be found in Appendix 2, Table A2.1.

	Units	Inlet Separator	Combined Waste Water (n=11)			
			Minimum	Maximum	Mean	Standard Deviation
Na	mg/L	14400	6780	14100	10368	2142
K	mg/L	440	8.33	385	194	109
Ca	mg/L	773	505	1030	710	171
Mg	mg/L	214	68	308	167	81
Fe	mg/L	14.50	4.30	193	53	58
Mn	mg/L	2.67	0.76	5.46	2	1
Cu	mg/L	0.02	0.001	0.81	0	0
Zn	mg/L	0.08	0.08	0.99	0	0
NH_3 (as N)	mg/L	35	0.56	43	15	12
pH	mg/L	7.6	5.6	8.4	7	1
Alkalinity (as HCO_3)	mg/L	512	293	622	414	106
Cl	mg/L	21400	11300	20000	16050	2765
Br	mg/L	97	25.6	177	91	44
SO_4	mg/L	1120	203	970	574	231
Turbidity	NTU	169	23.9	750	322	258
Conductivity	µS/cm	69600	22400	67000	52692	12761

The deep brine has higher concentrations of sodium (324x) than the domestic water samples but the sodium concentration of the deep brine is identical to seawater (Table 2). The calcium concentrations are 11.5x greater in the deep brine than the domestic water wells and 1.8x greater than seawater. Chloride concentrations are 336x greater in the deep brine compared to the domestic water samples and 0.85x those of seawater. Bromide concentrations are 479x higher in the deep brine compared to the domestic water wells and 1.4x greater than seawater. Sulfate concentrations are only 2x higher in the brine compared to the domestic water samples, and 0.2x the concentration in seawater.

Table 2 - Comparison of the deep brine chemistry to shallow groundwater chemistry.

Element	Mean Deep Brine (mg/L)	Mean Shallow Groundwater (mg/L)	Seawater (mg/L)	Ratio	
				Brine - SGW	Brine - SW
Na	10,368	32	10,556	324	0.98
K	194	2	380	97	0.51
Ca	710	62	400	11.5	1.78
Mg	167	4	1262	42	0.13
Alkalinity	414	67	140	6.2	3
Cl	16,050	48	18,980	336	0.85
Br	91	0.19	65	479	1.4
SO_4	574	270	2,680	2.1	0.2

Sedimentary basin brines are generally considered to be derived from seawater that has been modified by processes such as evaporation, diagenetic mineral-water reactions and redox reactions such as sulfate reduction (Hanor, 2001; Kharaka and Hanor, 2005; Milliken, 2005). The data suggest that the McCully field brine also originated from seawater and the differences that are noted can be explained by reaction processes related to burial and by uncertainty in the brine chemistry due to the inability to collect samples that are unaffected by the gas production plant.

3.2. McCully Gas

The production gas from the McCully Gas Field (produced by Corridor Resources Inc.) is dominantly comprised of methane (Table 3) with a methane mole fraction ranging from 0.91 – 0.94. The mole fraction of ethane and propane in the McCully gas ranges from 0.017 – 0.06 and 0.001 – 0.01 respectively.

Table 3 – Composition of gas from the McCully Gas Field (mole fraction).

Sample	Methane	Ethane	Propane
1	0.913	0.059	0.010
2	0.918	0.054	0.009
3	0.919	0.055	0.009
4	0.927	0.017	0.001
5	0.938	0.043	0.005
6	0.921	0.045	0.006

The hydrocarbon composition of the McCully Gas Field is comparable to other unconventional gas from North America with normalized methane compositions ranging from 79.80 – 99.89 % (Figure 5; Appendix 2 Table A2.2). Similarly, the ethane and propane compositions of the McCully field gas are within the range of ethane (0.11 – 16.18 %) and propane (0.00 – 5.30 %) in other North American unconventional gas fields.

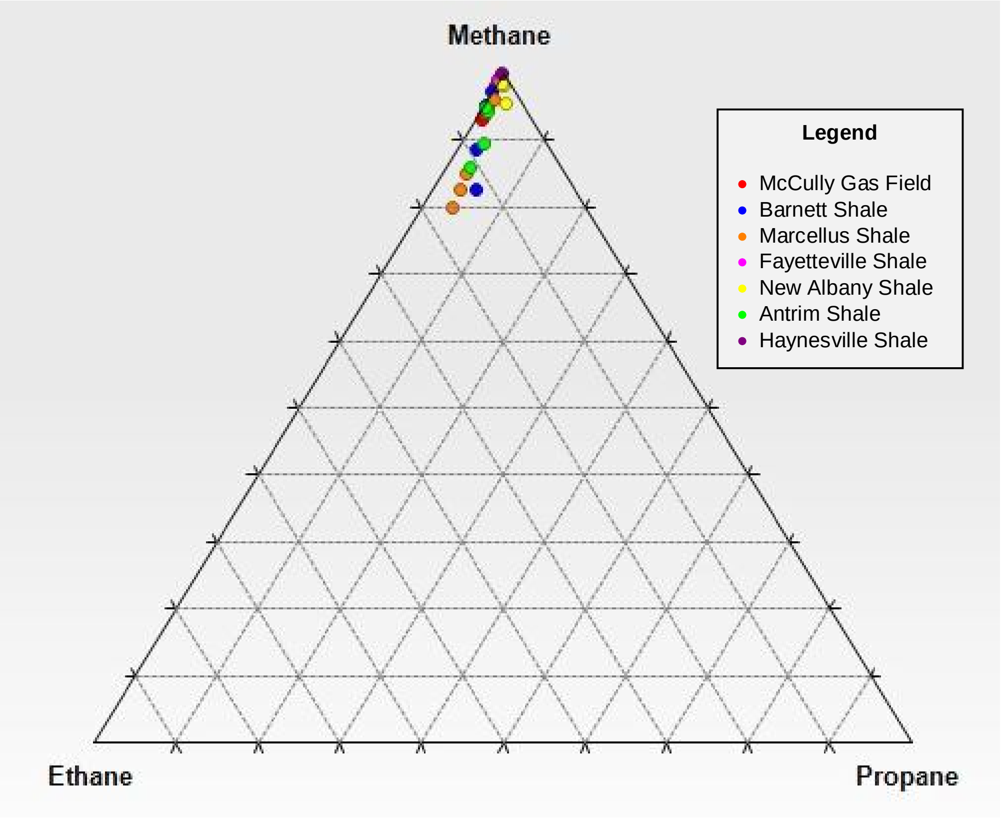

Figure 5. Relative concentrations of methane, ethane and propane in gas from North American unconventional gas fields (data from Bullin and Krouskop, 2009).

The isotopic composition of methane from McCully wells completed in the Hiram Brook Member sandstone (Figure 6) falls within the thermogenic field defined by Whiticar (1999), but samples from a well completed in the Frederick Brook shale are relatively enriched in δ^{13}C, plotting into the field defined by Whiticar (1999) for gas from geothermal, hydrothermal and crystalline rock environments. Despite their location on this variation diagram, it is not likely that the gas from the shale originates from a geothermal, hydrothermal or crystalline-rock environment, instead it more likely that the enrichment in δ^{13}C reflects an organic source with a greater component of terrigenous (type III) kerogen. It might be expected that the shale is the source of gas that is produced from the Hiram Brook sandstone, but that hypothesis is not consistent with these isotope data. Clearly additional work is required to explain the observed difference in gas isotopic composition between the Frederick Brook shale and the overlying Hiram Brook sandstone.

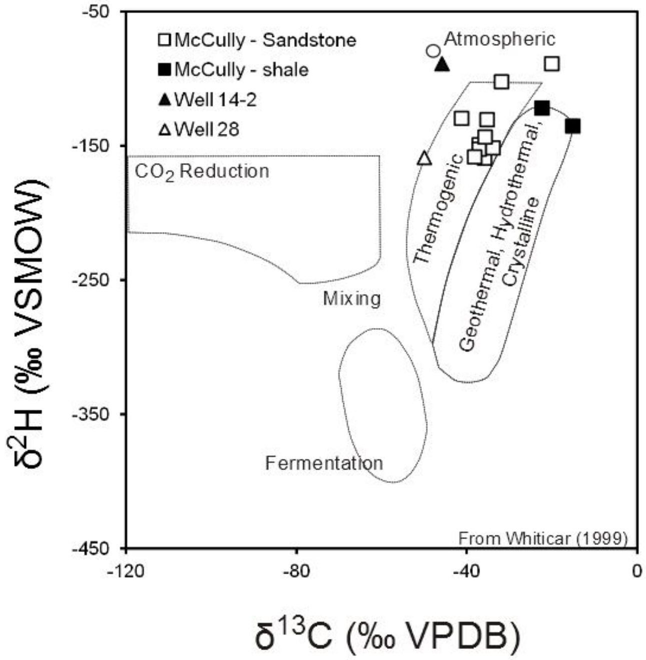

Figure 6. Isotopic composition of methane from the McCully Gas Field and from two samples of shallow groundwater.

3.3. Regional Shallow Groundwater

3.3.1. Inorganic Chemistry

A summary of the inorganic chemistry for samples of shallow groundwater is provided in Table 4 and the complete data are provided in Appendix 1, Table A1.1.

Table 4 – Summary of inorganic chemistry data for shallow groundwater.

	Minimum	Maximum	Mean	Standard Deviation	Guideline	Units
Na	2.48	302.9	32.3	61.9	200[a]	mg/L
Mg	0.07	20.8	4.0	4.7		mg/L
K	0.27	11.9	2.0	2.5		mg/L
Ca	0.01	561.9	62.2	105.1		mg/L
Al	0.77	17.6	5.6	5.9		µg/L
Mn	0.22	229.6	25.6	55.1	50[a]	µg/L
Fe	9.35	553.6	169.4	194.6	300[a]	µg/L
Sr	0.28	4224	933	1336		µg/L
As	0.37	168.5	19.5	47.4	10[b]	µg/L
Pb	4.2	26.6	11.0	5.2	10[b]	µg/L
Ba	0.24	869	215	228	1000[b]	µg/L
U	-	19.8	2.0	4.1	20[b]	µg/L
Cl	2.2	230	31.1	47.8	250[a]	mg/L
NO_3	0.23	21.1	3.6	4.9	10[b]	mg/L
SO_4	2.4	1334	103	270	500[a]	mg/L
Br	0.28	0.84	0.38	0.19		mg/L
pH	6.12	9.36	7.63	0.72	6.5 – 8.5[a]	
E_H	157	400	324	86		mV
Alkalinity[c]	22	333.6	133.6	67.4		mg/L

[a] aesthetic guideline: recommended that concentrations be less than this threshold
[b] maximum acceptable concentration
[c] alkalinity reported as HCO_3

The distribution of major-ion compositions for the shallow groundwater samples (Figure 7) is generally similar to the distribution for groundwater throughout New Brunswick (Rivard et al., 2008). Most of the water samples have a Ca-HCO_3 composition, but there is a trend toward Na-Cl type water (although the Na and Cl concentrations remain low compared to seawater; Table 2). When discussing the composition of New Brunswick groundwater in general, Rivard et al. (2008) suggested that the trend toward Na-Cl was due to the influence of seawater on coastal aquifers. However, the present study area is not located close to the present-day coastline and the trend toward Na-Cl type water cannot be explained by seawater intrusion. There are two natural sources that could explain the trend: 1) the localized occurrence of residual solutes from seawater in bedrock that originate from a time period approximately 10,000 years ago when sea level was higher than the present (Figure 8), and 2) residual solutes in Windsor Group rocks of marine origin. Contamination from surficial sources such as road salt could also explain the increases in Na and Cl concentrations. Samples collected within or near Windsor Group rocks (numbers 22 to 26) do not display anomalously high Na and Cl concentrations, so it is likely that the trend toward Na-Cl type water can be explained either by surficial contamination sources or by residual seawater from the last marine transgression.

The samples that define the trend toward Na-Cl type water contain the highest concentrations of Na and Cl; one of these (sample 10) contains sodium in excess of the aesthetic water quality guideline (Table 4) and is close to the aesthetic guideline for chloride. There are also results exceeding aesthetic guidelines for manganese, iron, sulfate and pH (Table 4). It is likely that these can be explained by the local geologic properties of the respective aquifers. There are several samples that exceed the maximum acceptable concentrations (MAC) defined by the New Brunswick government for arsenic, lead and nitrate (New Brunswick Department of Environment, 2008). The values exceeding MAC for arsenic are also attributable to the local geologic properties of the aquifers. The anomalous high lead values may reflect the geologic properties of the aquifer, but could also relate to lead sources in plumbing systems. The elevated nitrate reflects contamination from agricultural land use.

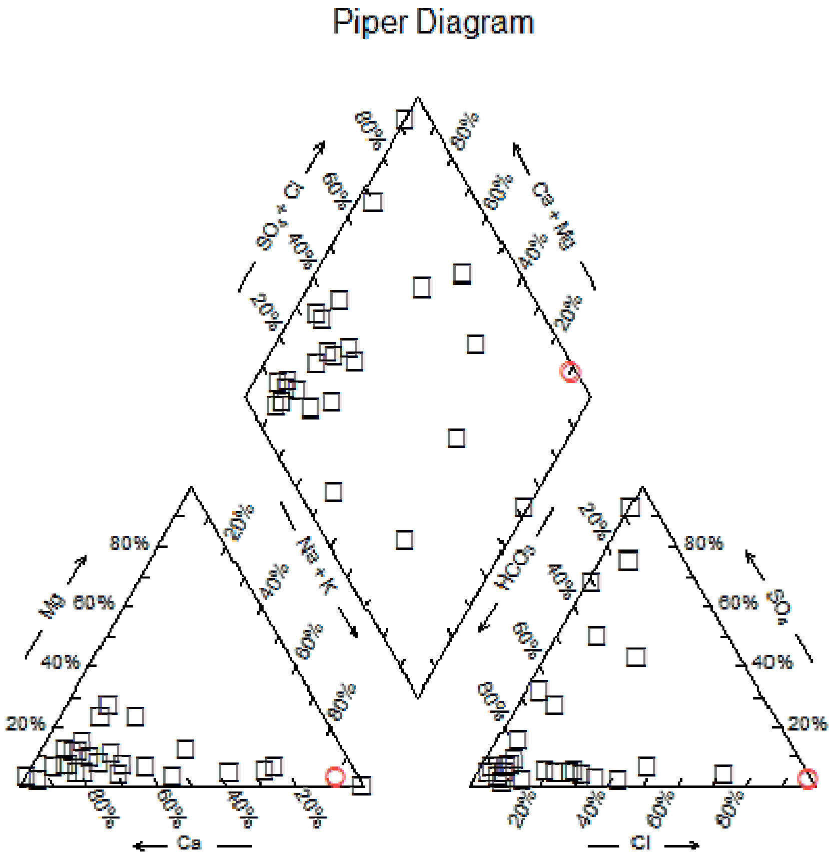

Figure 7. Piper diagram comparing the major-ion composition of the shallow groundwater (black squares) to the brine from the McCully Gas Field (red circles).

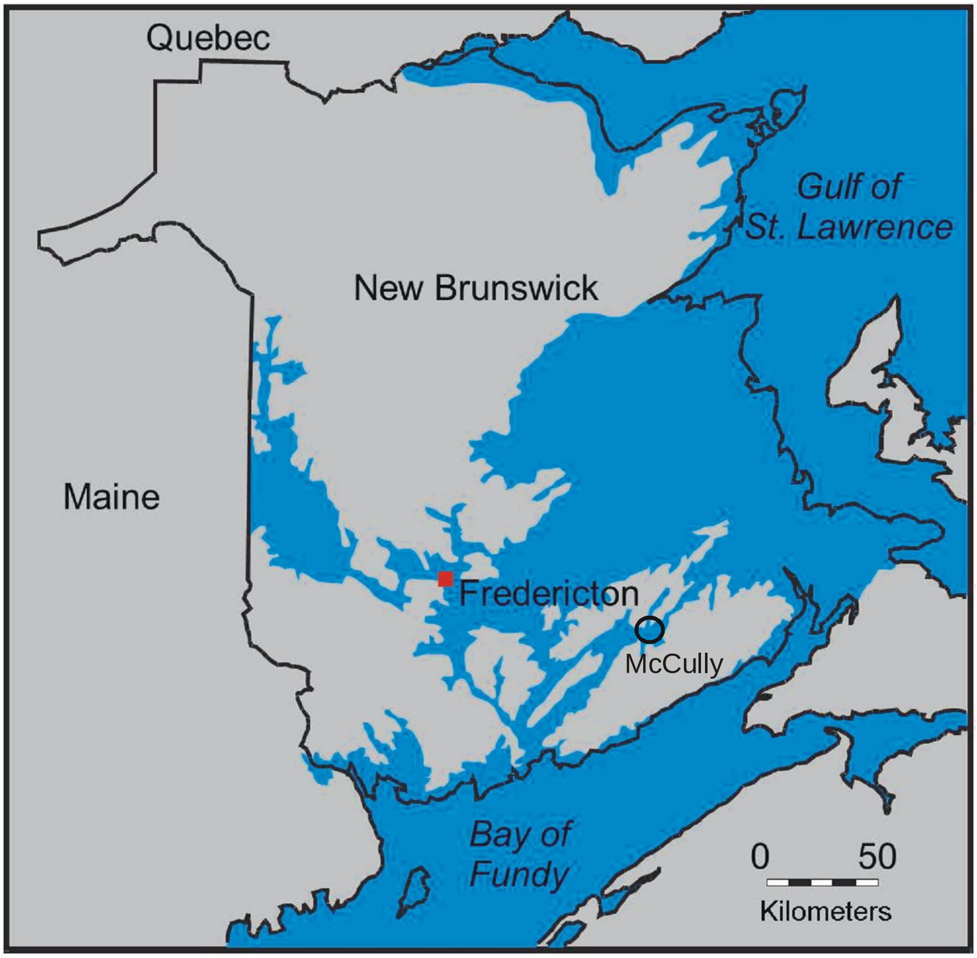

Figure 8. The Late Wisconsin marine limit in New Brunswick (Webb, 1981).

3.3.2. Water Isotopes

The water isotope data for shallow groundwater are presented in Figure 9. The global meteoric water line is shown for reference but two local meteoric water lines (LMWL) are also presented; one for Truro, Nova Scotia (Fritz et al., 1987) and one for Charlottetown (Francis, 1989). Most of the data cluster tightly around the Charlottetown LMWL suggesting that these groundwater samples represent recently recharged meteoric water. There is a small trend away from the LMWL toward enriched values for $\delta^{18}O$. This trend is typical of groundwater that has been subject to evaporation prior to recharge.

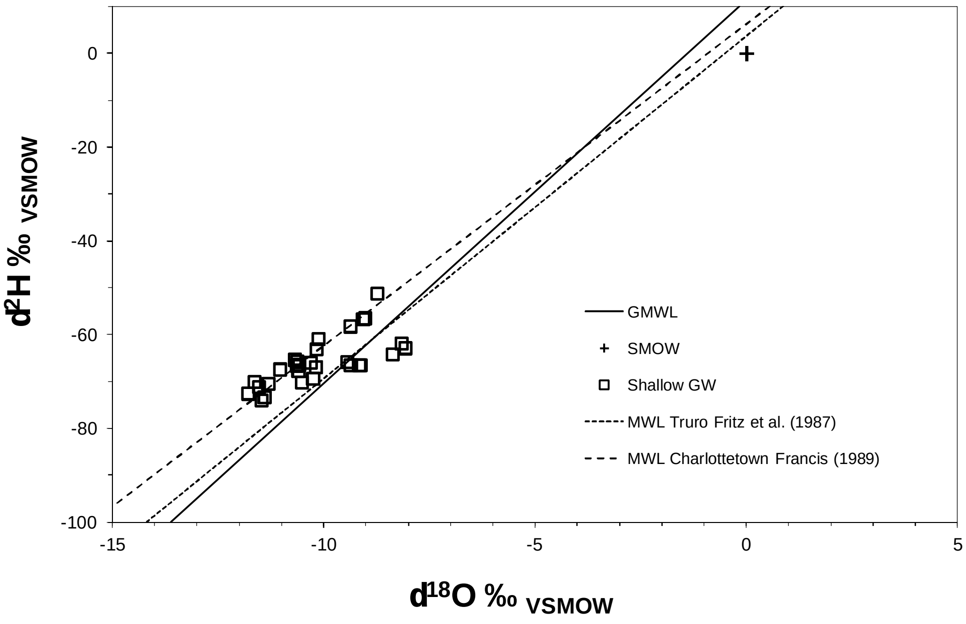

Figure 9. Water isotope data from shallow groundwater.

3.3.3. Dissolved Hydrocarbons

Methane was detected (detection limit – 0.01 mg/L) in only three of the domestic water well samples; ethane and propane were not detected (Figure 10). The amount of dissolved methane in the domestic water well samples ranged from <0.01 – 1.17 mg/L (Table 5). These are low concentrations compared to the solubility limit for methane in shallow freshwater aquifers (approximately 30 mg/L). There is no apparent spatial correlation between these detectable methane occurrences and known gas wells or production facilities.

Table 5 - Summary of dissolved hydrocarbon data for shallow groundwater (samples below detection limit not shown).

Sample	Methane (mg/L)	Ethane (mg/L)	Propane (mg/L)
9	0.01	N.D.	N.D.
14-2	0.11	N.D.	N.D.
28	1.17	N.D.	N.D.

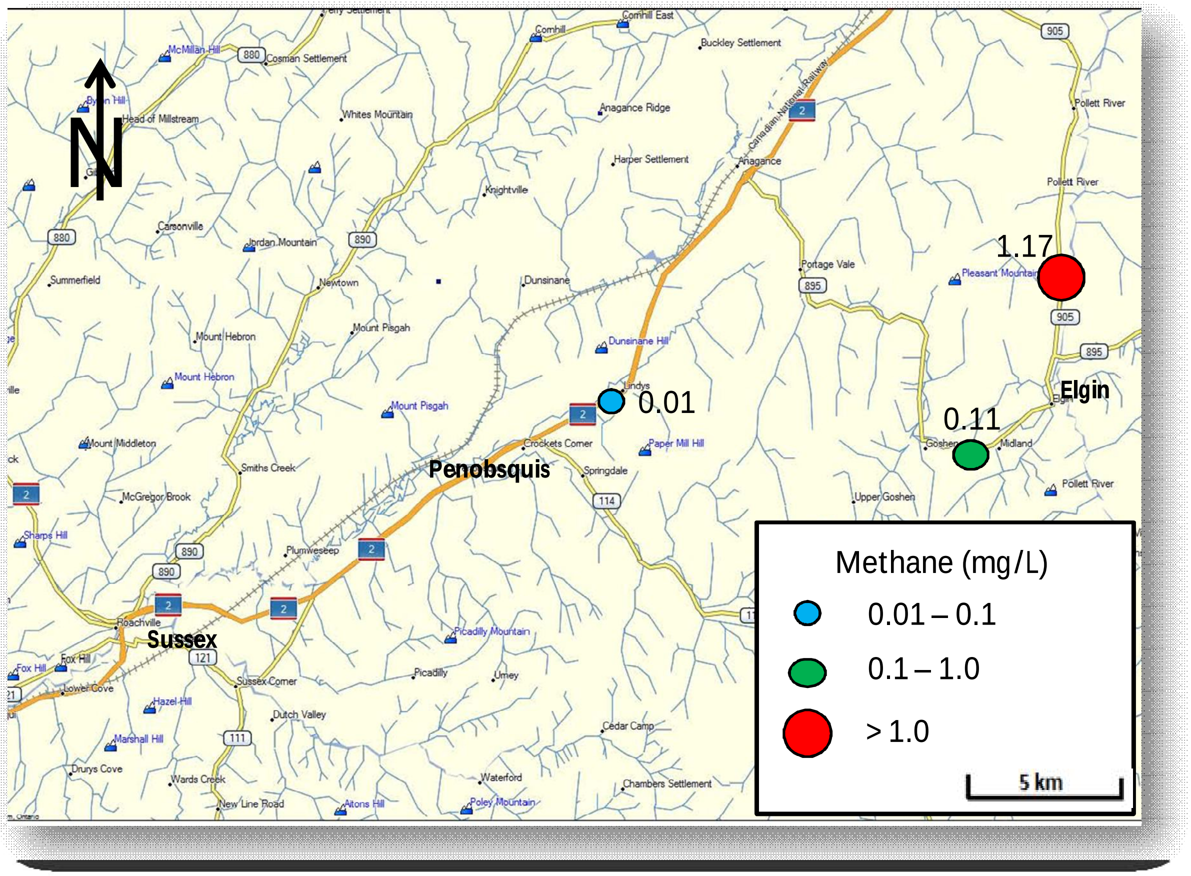

Figure 10. Location of samples with detectable dissolved methane in shallow groundwater.

The carbon and hydrogen isotope ratios of methane can help to identify its origin. There are two general types of methane, commonly referred to as biogenic and thermogenic. Biogenic methane is formed by low-temperature microbiological processes (CO_2 reduction and fermentation) in the near-surface environment and thermogenic methane is formed at temperatures in excess of 70°C (Hunt, 1996) from deeply buried organic-rich sedimentary rock – usually shale. Biogenic and thermogenic methane have distinct isotopic compositions (Whiticar, 1999; Figure 6). Isotopic measurements were conducted for two of the three samples with detectable methane. The isotopic composition of the third sample (sample 9) could not be measured because the methane concentration was too low.

The isotopic composition of sample 28 is clearly within the region defined by Whiticar (1999) for thermogenic gas, but the isotopic composition for sample 14-2 is relatively enriched in ^{2}H and plots outside the thermogenic field (Figure 6). Oxidation of methane with an initial isotopic composition in the thermogenic field, perhaps similar to sample 28, would cause enrichment of both ^{13}C and ^{2}H and could result in an isotopic composition similar to sample 14-2. This possible explanation is supported by the observed smell of H_2S gas during sampling at this home. Methane oxidation in groundwater is known to be microbiologically mediated, with CH_4 oxidation coupled to the reduction of SO_4, leading to the formation of H_2S (Van Stempvoort et al., 2005).

Based on communication with residents of the area, natural methane seeps, presumably from thermogenic sources, are known to occur in the Elgin area. These isotopic data suggest that the methane in samples 14-2 and 28 can be attributed to thermogenic sources.

4. Conclusions

A total of 26 domestic water well samples from an area around the McCully Gas Field and the town of Elgin, and samples of the gas and brine recovered from producing wells in the McCully field were collected and analyzed.

The inorganic chemical properties of the shallow groundwater samples are not unusual compared to New Brunswick groundwater in general. There are a few minor exceedances of the aesthetic water-quality guidelines for sodium, iron, manganese, sulphate and pH, and there are several samples that exceed the maximum acceptable concentrations (MAC) defined by the New Brunswick government for arsenic, lead and nitrate (New Brunswick Department of Environment, 2008). The exceeding arsenic values with respect to MAC are attributable to the local geologic properties of the aquifers. The anomalous higly lead values may reflect the geologic properties of the aquifer, but could also relate to lead sources in plumbing systems. The elevated nitrate reflects contamination from agricultural land use.

The water isotopes of the shallow groundwater samples are typical of recently recharged meteoric water.

Only three of the shallow groundwater samples (two near Elgin and one northeast of the McCully Gas Field) contained detectable methane, but at very low concentrations. None of the shallow groundwater samples contained detectable ethane or propane. There is no indication that gas development and production at the McCully Gas Field has affected the water wells that were sampled in this study.

The isotopes of methane indicate that the methane in two shallow groundwater samples from the Elgin area is of thermogenic origin. The detection of thermogenic gas in shallow wells in an area without commercial gas production demonstrates the importance of conducting comprehensive baseline sampling prior to gas exploration and development. Baseline sampling should include methane, ethane and propane analysis, and follow up should include analysis of methane isotopes for samples with detectable methane.

The inorganic chemistry of the deep brine from the McCully Gas Field indicates that the brine originated as seawater and has subsequently been slightly modified by diagenetic processes (dolomitization, ion exchange, sulphate reduction). The analysis of isotopes from the McCully Gas Field demonstrate that the gas is thermogenic, but samples from the Frederick Brook shale display unusual ^{13}C-enrichment, probably a reflection of a high type-III kerogen content in the shale.

5. Acknowledgements

We wish to thank all of the homeowners who allowed us to enter their homes and barns to collect samples. We also extend our appreciation to Corridor Resources who assisted with collection of water and gas samples, and provided analytical data from previous sampling events. Denis Lavoie (GSC-Q) is the scientific authority for this project and provided comments on an earlier manuscript. This study was funded by Natural Resources Canada through the Program of Energy Research and Development (PERD).

6. References

Bullin, K.A. and P.E. Krouskop. 2009. Composition variety complicates processing plans for US shale gas. Oil & Gas Journal, 107(10), 50 - 55.

Francis, R.M. 1989. Hydrogeology of the Winter River Basin, Prince Edward Island; Prince Edward Island Department of the Environment, Water Resources Branch, unpublished report, 117 p.

Fritz, P., Drimmie, R.J., Frape, S.K. and O'Shea, K. 1987. The isotopic composition of precipitation and groundwater in Canada: *in Isotope Techniques in Water Resources Development*; International Atomic Energy Agency, Symposium 299, March 1987, Vienna, Austria, 539-550.

Hanor, J.S., 2001. Reactive transport involving rock-buffered fluids of varying salinity. *Geochimica Cosmochimica Acta*, 65, 3721-3732.

Hea, S.P. 1974. Petroleum potential of the province of New Brunswick, Canada. Unpublished Report, Weaver Oil and Gas Corporation, p. 51.

Hinds, S. and C. St. Peter. 2005. The McCully Gas Field Project. http://www.gnb.ca/0078/minerals/PDF/McCully_Gas_Field_Project-e.pdf

Hunt, J. M., 1996, *Petroleum geochemistry and geology*. San Francisco, W. H. Freeman, 743 p.

Kargbo, D.M., R.G . Wilhelm and D.J. Campbell. 2010. Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities. *Environ. Sci. Technol.* 44*,* 5679–5684.

Kharaka, Y. K. and J.S. Hanor, 2005. Deep Fluids in the Continents: I. Sedimentary Basins, *In*: J.I. Drever (ed), *Surface and Ground Water, Weathering, and Soils: Treatise on Geochemistry*, Volume 5, Elsevier, NY. 499-540.

Kresse, T.M., Warner, N.R., Hays, P.D., Down, A., Vengosh, A and R.B. Jackson. 2011. Shallow groundwater quality and geochemistry in the Fayetteville shale gas-production area, north-central Arkansas. U.S. Geological Survey Scientific Investigations Report 2012–5273, 31 p. Retrieved on January 15, 2013 from: http://pubs.usgs.gov/sir/2012/5273/

Milliken, K.L., 2005. Late Diagenesis and mass transfer in sandstone-shale sequences. *In*: F.T. Mackenzie (ed.), *Sediments, Diagenesis, and Sedimentary Rocks: Treatise on Geochemistry, Volume 7*, Elsevier, NY, 159-190.

New Brunswick Department of Environment, 2008. New Brunswick Groundwater Chemistry Atlas: 1994-2007. Sciences and Reporting Branch, Sciences and Planning Division, Environmental Reporting Series T2008-01, 31p.

Rivard, C., Michaud, Y., Deblonde, C., Boisvert, V., Carrier, C., Morin, R.H., Calvert, T., Vigneault, H., Conohan, D., Castonguay, S., Lefebvre, R., Rivera, A. and Parent, M. 2008. *Canadian Groundwater Inventory: Regional Hydrogeological*

Characterization of the South-central Part of the Maritimes Basin. Geological Survey of Canada Bulletin 589, 96 p.

St. Peter, C. 2000. Oil shales and oil and natural gas in New Brunswick: Historical and current industry-related activities. New Brunswick Department of Natural and Energy, Minerals and Energy Division, Information Circular 2000-5, p.14.

Stefik, R. and K. Paulson. 2011. When Unconventional Becomes Conventional. *Journal of Canadian Petroleum Technology*, 50:(11-12), 68-70.

Van Stempvoort, D., H. Maathuis, E. Jaworski, B. Mayer, and K. Rich. 2005. Oxidation of Fugitive Methane in Ground Water Linked to Bacterial Sulfate Reduction. *Ground Water*, 43:(2), 187–199.

Webb, T.C. 1981. Origin of brackish formational ground waters in the Pennsylvanian of New Brunswick. New Brunswick Department of Natural Resources, Mineral Development Branch, Open File 82-5, 24 p.

Whiticar, M. J. 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chemical Geology*, 161: 291–314.

Appendix I

Table A1.1 - Inorganic geochemistry of shallow groundwater.

Element	Sodium	Magnesium	Aluminum	Potassium	Calcium	Vanadium	Chromium	Manganese
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Sample 2	114881	4998	1,0	6302	64874	1,7	<DL	<DL
Sample 3	7668	1254	0,9	492	124207	0,1	<DL	2
Sample 4	12434	1646	<DL	609	51187	0,5	1,1	3
Sample 5	115474	4791	3,1	1167	126234	1,9	<DL	0
Sample 6	16465	1245	<DL	2111	39081	2,9	1,2	1
Sample 7	5706	<DL	<DL	<DL	7	0,0	0,4	0
Sample 7a (duplicate)	8691	3291	<DL	1465	67248	6,5	<DL	1
Sample 8	23610	1310	2,0	6302	7679	<MDL	<DL	31
Sample 9	3048	3040	<DL	1129	33503	2,4	<DL	28
Sample 10	302863	69	10,3	11866	1491	14,6	<DL	2
Sample 11	4402	1515	<DL	666	30361	1,4	<DL	<DL
Sample 12	6778	2338	2,5	965	29382	0,5	<DL	1
Sample 12-2	5987	1536	3,3	2853	25103	0,6	<DL	14
Sample 13	2587	1527	<DL	468	5975	<MDL	<DL	0
Sample 14	9688	5139	1,7	1551	57736	1,5	<DL	2
Sample 14-2	31775	4948	<DL	1620	30451	0,4	<DL	32
Sample 15	7969	1389	17,6	825	40473	1,3	<DL	2
Sample 19	18840	20790	1,6	2921	95171	0,1	<DL	170
Sample 20	5428	3907	<DL	513	32039	<MDL	<DL	14
Sample 21	12790	15468	10,8	1184	55924	0,1	<DL	21
Sample 22	3855	2341	0,8	507	26986	0,5	<DL	1
Sample 23	4738	10553	14,2	302	561887	0,3	<DL	230
Sample 24	2478	691	<DL	266	7231	0,2	<DL	1
Sample 25	14670	2032	16,3	1197	33229	0,4	<DL	1
Sample 26	48305	4679	2,1	1358	76784	14,5	<DL	1
Sample 27	3094	1839	0,8	1978	42467	1,6	<DL	0
Sample 28	54594	2073	<DL	1073	18287	<MDL	<DL	57
Detection Limit (µg/L)	**5**	**0,4**	**0,6**	**9,5**	**6,9**	**0,02**	**0,2**	**0,2**

Table A1.1 - Inorganic geochemistry of shallow groundwater.

Element	Iron	Cobalt	Nickel	Copper	Zinc	Arsenic	Selenium	Strontium	Molybdenum
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Sample 2	<DL	0,1	0,4	3,3	0,3	0,5	<DL	706	0,3
Sample 3	28,8	0,1	0,5	2,1	3,2	<DL	<DL	1844	0,4
Sample 4	9,4	0,1	0,6	44,6	18,3	<DL	<DL	59	0,9
Sample 5	<DL	0,1	0,6	1,0	<DL	0,8	<DL	2692	0,6
Sample 6	<DL	0,1	0,3	9,8	1,6	0,6	<DL	166	1,4
Sample 7	<DL	0,1	<DL	4,2	12,0	<DL	0,7	0	0,4
Sample 7a (duplicate)	<DL	0,1	0,3	1,3	0,6	7,8	<DL	1422	0,8
Sample 8	35,5	0,0	0,2	<DL	8,0	0,5	<DL	46	0,9
Sample 9	272,0	0,1	1,6	<DL	<DL	1,8	<DL	530	0,5
Sample 10	46,0	<DL	2,6	0,2	46,7	168,5	<DL	29	29,7
Sample 11	<DL	0,1	0,1	5,7	1,0	<DL	<DL	216	0,3
Sample 12	<DL	0,3	0,4	134,3	5,8	<DL	<DL	49	0,2
Sample 12-2	<DL	0,0	1,0	6,2	1,3	<DL	<DL	237	0,3
Sample 13	<DL	0,7	0,1	74,7	2,1	<DL	<DL	8	0,1
Sample 14	<DL	0,1	0,3	29,5	1,0	0,6	<DL	636	0,3
Sample 14-2	13,8	0,1	0,2	<DL	<DL	0,8	<DL	1201	0,4
Sample 15	21,2	0,1	0,2	84,1	3,8	0,7	0,7	112	0,1
Sample 19	395,1	0,2	0,9	0,5	0,8	2,8	<DL	4218	5,4
Sample 20	433,4	0,1	0,7	1,2	8,0	<DL	<DL	95	1,1
Sample 21	54,7	0,1	1,0	2,1	3,1	91,1	<DL	4224	14,8
Sample 22	<DL	0,2	0,7	5,1	1,5	<DL	<DL	77	0,2
Sample 23	553,6	0,5	2,7	1,7	12,5	<DL	<DL	3719	0,4
Sample 24	<DL	0,0	0,1	52,2	1,1	<DL	0,8	16	0,3
Sample 25	<DL	0,2	0,7	300,1	3,7	0,4	1,0	43	0,2
Sample 26	<DL	0,1	0,6	6,6	6,1	3,0	2,2	2313	28,1
Sample 27	<DL	0,1	0,4	7,9	6,0	0,6	<DL	862	0,1
Sample 28	<DL	<DL	<DL	<DL	<DL	<DL	<DL	166	0,5
Detection Limit (µg/L)	**5,2**	**0,02**	**0,1**	**0,2**	**0,1**	**0,3**	**0,5**	**0,02**	**0,1**

Table A1.1 - Inorganic geochemistry of shallow groundwater.

Element	Antimony	Barium	Lead	Thorium	Uranium	Bromine	Chlorine	Fluorine
	µg/L	µg/L	µg/L	µg/L	µg/L	mg/L	mg/L	mg/L
Sample 2	<DL	191	13	<DL	1,2	0,29	230,22	0,20
Sample 3	<DL	10	10	<DL	0,5	N/A	4,28	0,28
Sample 4	1,8	279	12	0,03	0,1	N/A	36,21	0,19
Sample 5	<DL	10	4	<DL	3,9	N/A	37,90	0,20
Sample 6	1,0	327	23	<DL	2,6	N/A	18,18	0,21
Sample 7	0,6	0	13	<DL	<MDL	0,29	6,87	0,21
Sample 7a (duplicate)	0,4	383	6	<DL	5,9	N/A	N/A	N/A
Sample 8	0,3	20	8	<DL	0,01	N/A	5,55	0,37
Sample 9	0,2	227	9	<DL	3,1	N/A	5,71	0,21
Sample 10	<DL	11	8	<DL	19,8	N/A	64,43	0,89
Sample 11	<DL	146	7	<DL	0,7	N/A	5,39	0,21
Sample 12	0,2	407	10	<DL	0,5	N/A	17,35	0,19
Sample 12-2	<DL	381	8	<DL	1,3	N/A	17,31	0,18
Sample 13	<DL	7	9	<DL	<MDL	N/A	2,35	0,23
Sample 14	<DL	674	11	<DL	0,8	N/A	9,29	0,23
Sample 14-2	<DL	869	5	<DL	0,4	0,29	11,19	0,34
Sample 15	<DL	76	8	<DL	0,4	N/A	13,83	0,19
Sample 19	<DL	472	7	<DL	1,4	0,30	112,49	0,26
Sample 20	<DL	100	9	<DL	0,2	0,28	2,31	0,22
Sample 21	<DL	154	27	<DL	2,2	N/A	6,54	0,41
Sample 22	<DL	340	13	<DL	0,2	N/A	5,26	0,23
Sample 23	<DL	18	19	<DL	0,0	N/A	3,56	0,49
Sample 24	0,3	62	17	<DL	0,0	N/A	2,17	0,25
Sample 25	0,2	104	11	<DL	0,1	N/A	32,87	0,18
Sample 26	1,5	10	13	0,03	8,2	0,84	66,60	0,55
Sample 27	<DL	576	5	<DL	0,7	N/A	26,62	0,22
Sample 28	<DL	108	7	<DL	0,004	0,39	64,94	0,42
Detection Limit (µg/L)	**0,1**	**0,1**	**0,02**	**0,02**	**0,003**	**0,71**	**0,69**	**0,55**

Table A1.1 - Inorganic geochemistry of shallow groundwater.

Element	Nitrate mg/L	Phosphate mg/L	Sulfate mg/L	Bicarbonate mg/L
Sample 2	11,51	N/A	15,05	132,21
Sample 3	0,64	N/A	223,07	125,90
Sample 4	3,04	0,10	6,86	137,70
Sample 5	1,91	N/A	441,17	119,60
Sample 6	2,80	N/A	6,60	119,60
Sample 7	1,89	N/A	64,60	164,75
Sample 7a (duplicate)	N/A	N/A	N/A	N/A
Sample 8	N/A	N/A	17,34	109,83
Sample 9	N/A	N/A	4,38	109,22
Sample 10	0,23	N/A	345,86	333,57
Sample 11	1,21	N/A	5,78	103,53
Sample 12	1,39	N/A	4,37	96,00
Sample 12-2	0,73	N/A	4,49	71,80
Sample 13	0,40	N/A	7,68	21,97
Sample 14	6,69	N/A	5,26	202,89
Sample 14-2	N/A	N/A	2,36	188,65
Sample 15	6,61	N/A	2,41	136,27
Sample 19	N/A	N/A	5,15	252,82
Sample 20	0,23	N/A	3,35	96,21
Sample 21	1,19	N/A	15,39	269,09
Sample 22	1,78	N/A	6,05	91,12
Sample 23	N/A	N/A	1334,15	128,75
Sample 24	0,31	N/A	3,08	36,20
Sample 25	3,05	N/A	2,80	97,63
Sample 26	9,44	N/A	134,26	128,55
Sample 27	21,10	N/A	4,21	95,19
Sample 28	0,39	N/A	11,62	104,34
Detection Limit (µg/L)	**0,23**	**0,2**	**1,23**	

Table A1.2 - Hydrocarbon content in shallow groundwater.

Sample	Dissolved in Water		
	Methane (mg/L)	Ethane (mg/L)	Propane (mg/L)
2	<0.01	N.D.	<0.01
2-Duplicate	<0.01	<0.01	<0.01
3	<0.01	<0.01	<0.01
4	<0.01	<0.01	<0.01
5	<0.01	N.D.	N.D.
5-Duplicate	<0.01	N.D.	N.D.
6	<0.01	<0.01	<0.01
7	<0.01	<0.01	<0.01
8	<0.01	N.D.	N.D.
9	0,01	N.D.	N.D.
10	<0.01	N.D.	N.D.
11	<0.01	N.D.	N.D.
12	<0.01	<0.01	<0.01
12-2	<0.01	N.D.	<0.01
13	<0.01	<0.01	<0.01
14	<0.01	N.D.	<0.01
14-2	0,11	N.D.	N.D.
15	<0.01	N.D.	<0.01
20	<0.01	N.D.	<0.01
21	<0.01	N.D.	<0.01
22	<0.01	<0.01	<0.01
22-Duplicate	<0.01	<0.01	<0.01
23	<0.01	N.D.	N.D.
24	<0.01	N.D.	N.D.
25	<0.01	N.D.	<0.01
26	<0.01	N.D.	<0.01
27	<0.01	<0.01	<0.01
28	1.17	N.D.	N.D.

Table A1.3 - Water isotopes in shallow groundwater.

Sample	δ^2H	δ^{18}O
2	-62,83	-8,08
3	-64,12	-8,38
4	-61,86	-8,17
5	-66,47	-9,17
5-Duplicate	-66,46	-9,14
6	-66,5	-9,37
7	-65,77	-9,45
8	-69,37	-10,26
9	-70,15	-10,53
10	-65,93	-10,32
11	-73,28	-11,41
11-Duplicate	-74	-11,48
12	-70	-11,65
12-2	-71,12	-11,54
13	-67,36	-11,04
14	-66,38	-10,59
14-2	-70,4	-11,32
15	-58,2	-9,38
19	-60,84	-10,13
20	-63,04	-10,18
21	-56,45	-9,03
21-Duplicate	-56,68	-9,08
22	-66,58	-10,65
23	-67,64	-10,61
24	-65,3	-10,69
25	-51,16	-8,74
26	-65,7	-10,63
27	-66,84	-10,19
28	-72,52	-11,8

Table A1.4 - Methane isotopes in shallow groundwater.

Sample	δ^{13}C	δ^2H
Water Well 14-2	-45,84	-88,39
Water Well 28	-49,96	-158,32

Appendix II

Table A2.1 - Water chemistry of brine produced from gas wells.

		Sodium mg/L	Potassium mg/L	Calcium mg/L	Magnesium mg/L	Iron mg/L	Manganese mg/L	Copper mg/L	Zinc mg/L
Sample 1	Tank	11200	120	716	148	22,6	2,14	0,04	0,137
Sample 2	Tank	8660	91,3	558	146	7,04	1,15	0,001	‹ 0.001
Sample 3	Tank	9190	188	936	199	54,7	2,01	< 0.01	0,08
Sample 4	Tank	9780	234	707	137	193	4,00	0,10	0,32
Sample 5	Tank	6780	176	722	101	78,1	1,42	0,363	0,990
Sample 6	Tank	11500	266	1030	250	57,4	2,88	0,04	0,13
Sample 7	Tank	12500	358	569	302	136	5,46	0,81	0,72
Sample 8	Tank	14100	385	526	308	41,9	2,92	0,11	0,2
Sample 9	Tank	11600	203	791	146	25,5	1,79	0,055	0,196
Sample 10	Tank	12100	203	874	121	12,1	0,797	0,022	0,327
Sample 11	Tank	7800	8,33	505	68	4,3	0,76	< 0.01	0,11
Sample 12	Tank	9200	95,1	591	75,6	6,2	0,97	< 0.01	0,09
Sample 13	Inlet Separator	14400	440	773	214	14,5	2,67	0,02	0,077

Table A2.1 - Water chemistry of brine produced from gas wells.

	Ammonia (as N)	pH	Alkalinity (as CaCO3)	Chloride	Bromine	Sulfate	Turbidity	Conductivity
	mg/L		mg/L	mg/L	mg/L	mg/L	NTU	µS/cm
Sample 1	15	6,3	360	19100	73	560	74	57100
Sample 2	17	7,5	270	15100	67	390	115	46000
Sample 3	5,9	7,7	440	14000		530	559	58400
Sample 4	0,56	8,0	344	16800	58,9	203	157	55200
Sample 5	4,2	8,4	388	11300	25,6	470	502	22400
Sample 6	2	8	300	15000	75,7	550	540	63200
Sample 7	43	8,3	510	20000	140	700	750	62100
Sample 8	16	6,9	430	19700	142	330	630	67000
Sample 9	15	7,7	300	14 500	68	950	256	49 200
Sample 10	25	5,6	240	18 500	177	970	230	65 300
Sample 11	16,6	7,8	250	13 300	84	510	31,9	40 400
Sample 12	16,1	7,5	250	15 300	89	730	23,9	46 000
Sample 13	35	7,6	420	21 400	97	1 120	169	69 600

Table A2.2 - McCully gas field hydrocarbon composition.

Sample Location	Methane (Mole Fraction)	Ethane (Mole Fraction)	Propane (Mole Fraction)
McCully Gas Field – B-58	0,913	0,0588	0,0102
McCully Gas Field – O-66	0,918	0,0544	0,0089
McCully Gas Field – M66	0,919	0,0548	0,0086
McCully Gas Field – F58	0,927	0,017	0,0012
McCully Gas Field – J38	0,938	0,0425	0,0052
McCully Gas Field – D48	0,921	0,0445	0,0062

Table A2.3 - McCully gas field methane isotopes.

Sample	**$\delta^{13}C$**	**$\delta^{2}H$**
Gas Well B-58	-37,17	-148,65
Gas Well B-58	-35,87	-158,98
Gas Well B-58	-35,78	-143,28
Gas Well D-48	-35,26	-129,99
Gas Well F-58	-15,15	-135,05
Gas Well F-58	-22,44	-121,72
Gas Well J-38	-37,19	-151,98
Gas Well J-38	-33,95	-151,18
Gas Well J-38	-38,2	-157,87
Gas Well M-66	-31,93	-102,09
Gas Well M-66	-20,13	-88,67
Gas Well M-66	-41,26	-129,28