Establishing baseline concentration and δ^{13}C signature of methane in

shallow ground waters of the St. Lawrence Lowlands, QC, Canada:

A tool for determining shale gas contamination

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Abstract

Establishing baseline concentration and δ^{13}C signature of methane in shallow ground waters of the St. Lawrence Lowlands, QC, Canada: A tool for determining shale gas contamination

Anja Miriam Moritz

With the increased interest in non-conventional energy sources, major environmental questions are being raised concerning the possible impacts of shale gas exploitation on the quality of ground waters. The extraction of shale gas is done by hydraulic fracturing, which utilizes large volumes of water and fracturing fluids to break the source rocks that entrap gases such as methane, ethane and propane. Because it is uncertain whether these fracturing fluids and gases can contaminate shallow ground waters, it is important to assess the baseline concentration of these gases before hydraulic fracturing activities are initiated to be able to determine the source of future ground water contaminations. In this work, we measured the natural concentrations and sources of hydrocarbons dissolved in ground waters of the St. Lawrence Lowlands, QC, Canada, in 130 ground water samples collected from private (n=81), municipal (n=34) and observation (n=15) wells. Localized pools of high concentrations of methane of mostly bacterial origin (biogenic) were found throughout the study area. Three samples showed high concentrations of methane bearing a δ^{13}C signature specific to

deep sources (thermogenic) but a gas wetness ratio ($C_1/(C_2+C_3)$) falling outside the

thermogenic gas window. This result suggests mixing with gas from other sources,

migration through the bedrock, or partial oxidation of the gas. The results obtained in

this study will be used as a reference for future research projects and monitoring

activities on the impact of shale gas exploration and exploitation on ground water

quality.

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Contribution of authors

All analyses were carried out by A. Moritz under the supervision of Y. Gélinas and J.-F. Hélie. They were completed at Concordia University (all concentration and isotopic measurements) and at the Université du Québec à Montréal (calibration of the reference gases for stable carbon isotope measurements). Fieldwork and collection of samples were done by A. Moritz, S. Retailleau and D. Barnetche, with occasional help from students from Concordia University and UQAM. The figures and tables were created by A. Moritz, with help from S. Retailleau and D. Barnetche. The project was coordinated by D. L. Pinti and M. Larocque (both from UQAM).

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List of acronyms

^{12}C	Carbon 12
^{13}C	Carbon 13
BAPE	*Bureau d'Audiences Publiques sur l'Environnement* or Office of Public Hearings on the Environment
Bcm	Billion cubic meters
C_2	Ethane
C_3	Propane
C_1	Methane
EIA	Energy Information Agency
EPA	Environmental Protection Agency
GC-C-IRMS	Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometry
GC-FID	Gas Chromatography-Flame Ionization Detector
GHG	Greenhouse Gas
KIE	Kinetic Isotope Effect
MDDEFP	*Ministère du Développement durable de l'Environnement, de la Faune et des Parcs* or Ministry of Sustainable Development, Environment, Wildlife and Parks
NY	New York
PA	Pennsylvania
PACES	Programme d'acquisition de connaissance des eaux souterraines
POTW	Publicly Owned Treatment Works

PDB	Pee Dee Belemnite
QC	Québec
SEA	Strategic Environmental Assessment
SMOW	Standard Mean Ocean Water
Tcm	Trillion cubic meters
TDS	Total Dissolved Solid
US	United States
USGS	United States Geological Survey
δ^{13}C	Stable carbon isotopic signature
δD	Stable hydrogen isotopic signature

1 General introduction

1.1 Natural gas

1.1.1 Natural gas: a fossil fuel

Natural gas is a fossil fuel derived from kerogen and an economically important energy source. Kerogen is the largest organic matter (OM) pool on Earth. Trapped in the bedrock, it accounts for 10^{16} tons of carbon derived mainly from terrestrial plant materials and algae.[1] It is mainly composed of carbon, hydrogen and oxygen and can be divided into three classes: Types I, II and III kerogen, which differ in their H/C and O/C molar ratios as well as the source of OM that led to its formation upon maturation. As the maturity of sedimentary organic matter increases after deposition on the seafloor, it is subjected to high pressure and temperature that results in major loss of nitrogen (early diagenesis), oxygen (diagenesis), hydrogen and carbon (catagenesis: formation of oil and wet gas) and finally in the reorganization of the remaining OM (metagenesis: formation of dry gas, mainly methane).[1]

In 2010, fossil fuels accounted for over 85% of the total energy production in Canada, with natural gas accounting for 36.5%[2] (Table 1.1). It is speculated that we are entering a "Golden Age of Gas" in which natural gas will play a key role in our energy demands and will slowly replace other fossil fuels.[3] Projections by the US EIA estimate that the natural gas production in the US will increase by 56% from 2012 to 2040 and that natural gas will account for 35% of the total electricity generation in 2040.[4] This increase in natural gas production is partly due to the growing interest in unconventional natural gas.

Table 1.1: Canada's produced energy in 2010 (from Natural Resources Canada[2])

Energy source	Percentage of total energy production (%)
Crude oil	41.4
Natural gas	36.5
Coal	9.2
Renewable energies	11
Nuclear	1.9

1.1.2 Conventional *vs.* unconventional natural gas

After its formation, conventional natural gas usually escapes its source rock and migrates through permeable rock formations until it reaches an impermeable rock, or seal, where it accumulates and forms a reservoir.[5] To extract this gas, a vertical well is usually drilled to tap into the gas reservoir (Figure 1.1). Natural gas, whether conventional or unconventional, is mainly composed of methane (70-90%) but also contains higher hydrocarbon gases such as ethane and propane, carbon dioxide, nitrogen, hydrogen sulphide and rare gases (Table 1.2).[6]

Natural gas is typically referred to as unconventional when the permeability of the source rock is lower than $9.87 \times 10^{-17}\,m^2$.[7] It can be defined as "natural gas that cannot be produced at economic flow rates nor in economic volumes of natural gas unless the well is stimulated by a large hydraulic fracture treatment, a horizontal wellbore, or by using multilateral wellbores or some other technique to expose more of the reservoir to the wellbore".[8] Unconventional gases comprise shale gas, coal-bed methane, tight gas

and gas hydrates[7,9] and unlike conventional natural gas its source and reservoir are the same.
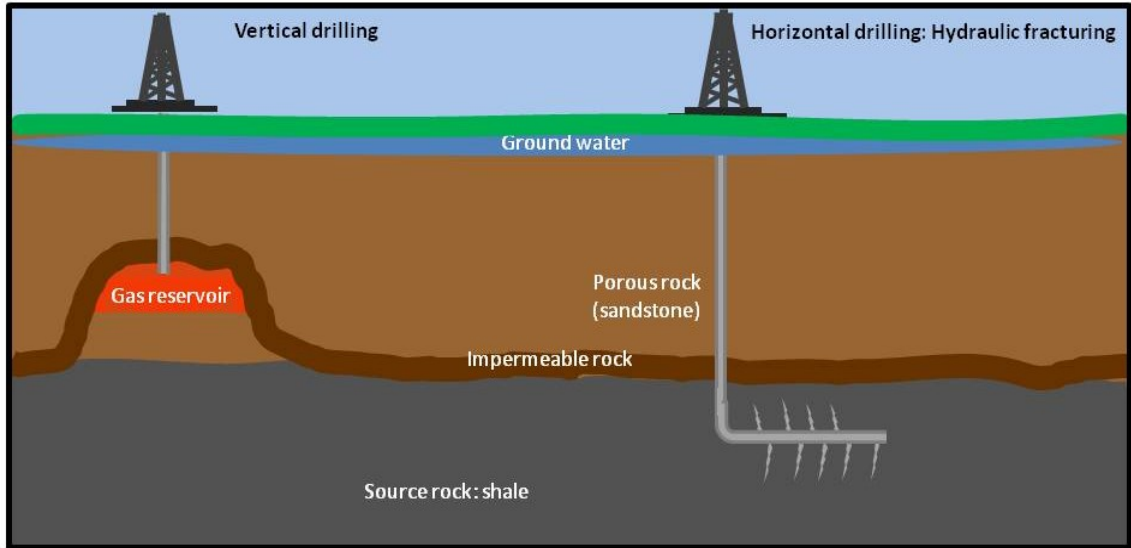
Figure 1.1: Conventional *vs.* unconventional natural gas recovery

Table 1.2: Composition of natural gas (modified from reference 6)

Gas	Percent of total natural gas (in %)
Methane	70-90
Higher hydrocarbon gases	0-20
Carbon dioxide	0-8
Oxygen	0-0.2
Nitrogen	0-5
Hydrogen sulphide	0-5
Rare gases (Ar, He, Ne, Xe)	Trace

1.1.3 Shale gas

1.1.3.1 What is shale gas

Shale is a sedimentary rock mainly composed of clay and silt. The Utica shale, which is the main shale formation in Quebec targeted for natural gas production, is composed of calcareous black mudstone.[10] Shales are rich in organic matter (as much as 50 wt%) although they contain lower organic matter concentrations than coal and other sedimentary rocks.[11] Gas is produced in the shale by bacteria to produce biogenic gas at shallow depths, or by the breakdown of the organic matter as the temperature and pressure of the shale increases, leading to the production of thermogenic gas.[5,11] Because of the low permeability of shales, which cover a very large horizontal area, the gas remains trapped in its pores, adsorbed onto organic matter or clays, or dissolved in the organic matter[5] rather than accumulating in a reservoir. The interest in shale gas is increasing worldwide and even though Canada is still at the early stages of shale gas production, over 1100 wells have been drilled as of 2012 for shale gas exploration or exploitation.[12]

1.1.3.2 Recoverable shale gas resources

A study conducted by the US Energy Information Administration (EIA) in 2013 assessed the technically recoverable shale gas resources in 41 different countries other than the US.[13] The expression "technically recoverable resources" refers to "gas estimated to be producible with current technologies ignoring economic constraints".[9] Their study showed a total of technically recoverable shale gas resources of 206.7 Tcm (including the US) with China in first place (31.6 Tcm) and Canada in 5th (16.2 Tcm),

Canada and the US being the only countries to produce shale gas in commercial quantities.[13] Table 1.3 lists the technically recoverable shale gas resources of 9 of the 41 assessed countries (plus the US) based on their findings.

Table 1.3: Technically recoverable shale gas resources in Tcm (modified from reference 13)

Rank	Country	Shale gas (Tcm)
1	China	31.6
2	Argentina	22.7
3	Algeria	20.0
4	US	18.8
5	Canada	16.2
6	Mexico	15.4
7	Australia	12.4
8	South Africa	11.0
9	Russia	8.1
10	Brazil	6.9
	World Total	206.7

Canada has 8 basins that contain shale gases, 5 of which are found in Western Canada where drilling activity has already started and produced 161.3 Bcm of natural gas in 2009.[14] Compared to the US however, where horizontal drilling started in the

1980s,[13] the shale gas "boom" has not yet occurred in Canada. In the US, shale gas accounted for 23% of the total natural gas production in 2010[15] whereas only 5% of the natural gas produced in Canada in 2010 came from unconventional sources.[12] The slow growth of shale gas extraction in Canada can be explained by moratoria in Quebec and Newfoundland and Labrador, as well as by the willingness of the Canadian population to impose a nationwide "national fracking moratorium",[16] where "fracking" refers to the shale gas extraction technique.

1.1.3.3 History of shale gas in Quebec

Eastern Canada is at its early stages of shale gas exploration in the Utica and Lorraine shales (Quebec), the Horton Bluff shale (Nova Scotia) and the Frederick Brook shale (New Brunswick).[14] In Quebec, the discovery of natural gas dates back to the 19th century and the first horizontal wells were drilled as early as 1971.[12] However, the interest in exploring the Utica shale only grew in 2006 when multiple wells were drilled to assess its production potential. Until 2011, 31 exploration drilling permits had been issued in Quebec, and 18 of these permits allowed hydraulic fracturing for exploration.[17] The hydraulic fracturing activities in Quebec and elsewhere (mostly in the US) resulted in a broad protest movement from the Quebec population and the involvement of the Office of Public Hearings on the Environment (BAPE) in 2010.[12]

The BAPE was mandated to enquire on the sustainable development of the shale gas industry in Quebec. Their report only partially answered important questions regarding the impact of hydraulic fracturing in Quebec and concluded that hydraulic fracturing should only be permitted under strict conditions.[18] Following the submission

of this report, exploration drilling was stopped, leading to the implementation of a moratorium.

In 2011, the Ministry of Sustainable Development, Environment, Wildlife and Parks (MDDEFP) created a Strategic Environmental Assessment (SEA; http://ees-gazdeschiste.gouv.qc.ca/en/) on shale gas committee to help answer environmental and socio-economical questions regarding the development of shale gas in Quebec as well as propose guidelines for regulations.[19] This Masters' project, along with a project on rare gases conducted at UQAM, was part of this environmental assessment. The fieldwork and analyses were completed at the end of the summer of 2013, and a full report was submitted to the SEA committee in August 2013. The document reporting our study was made available online in September 2013,[20] and the final SEA report, comprising all the studies launched as part of the SEA, was made available to the public in January 2014.[21] Note that I actively participated in the writing of the report, particularly for the sections directly pertaining to shale gas sampling, measurements and data interpretation.

1.2 Shale gas extraction

Shale gas extraction is achieved by using hydraulic fracturing which consist of drilling a horizontal well at a depth of around 2400 to 3000 m[7] (Figure 1.1).

1.2.1 Hydraulic fracturing

Hydraulic fracturing has been used in conventional oil and gas well drilling to increase reservoir permeability[5] and is now used in horizontal drilling for shale gas

exploitation. Unlike conventional gas drilling where typically only one gas well is drilled

per 2.6 km (in Western Canada), unconventional gas drilling requires as many as 8 gas

wells per site to ensure maximum connectivity in the shale rock.[5] The rock is fractured

by pumping large amounts of water (>90% of total volume; Table 1.4) at high pressure

into the well. Each well requires about 7.6 to 15.1 million liters of water[22] and costs

about 3 to 5 million USD[23] depending on its size and gas resources. Proppant (usually

sand) is added to the water to keep the resulting fractures open, as well as a number of

chemicals.[7,23]

Colborn et al. (2011) identified 632 chemicals that are used in drilling

operations.[24] Some of the most important ones (by volume %) are acids to dissolve the

mineral matrix, gels and surfactants to increase fluid viscosity, corrosion inhibitors or

biocides[25] (Table 1.4). These additives along with the water and proppant are referred

to as fracturing fluids and their regulation is excluded by the Safe Drinking Water Act in

the US,[23] which means their composition is not disclosed to the public.

Table 1.4: Components of fracturing fluids used in horizontal drilling (modified from EPA, 2011[25])

Component	Typical Compound(s)	Purpose	Percent Composition (by volume)
Water		Deliver proppant	90
Proppant	Silica, quartz sand	Keeps fractures open to allow gas outflow	9.51
Acid	Hydrochloric acid	Dissolves minerals, initiate cracks in the rock	0.123
Friction reducer	Polyacrylamide, mineral oil	Minimizes friction between fluid and the pipe	0.088
Surfactant	Isopropanol	Increases the viscosity of the fluid	0.085
Gelling agent	Guar gum, hydroxyethyl cellulose	Thickens the fluid to suspend the proppant	0.056
Cross-linker	Borate salts	Maintains fluid viscosity as temperature increases	0.007
Iron control	Citric acid	Prevents precipitation of metal oxides	0.004
Corrosion inhibitor	N,N-dimethyl formamide	Prevents pipe corrosion	0.002
Biocide	Glutaraldehyde	Eliminates bacteria	0.001

1.2.2 Environmental concerns

The extraction of shale gas, although potentially beneficial to the economy because it promotes job creation and results in lower natural gas prices, can have major impacts on the quality of the environment and on public health.[7]

1.2.2.1 GHG emissions

Natural gas, upon combustion, is more efficient in producing energy compared to oil and coal and hence generates around 29% and 44% less carbon dioxide than oil and coal respectively when the same amount of energy is produced (Table 1.5). However these numbers do not take into account the full life cycle of the energy source, i.e. emissions during drilling, leaking, transportation, etc. Also, natural gas emits less nitrogen oxide, sulfur dioxide, and mercury than oil and coal for the same amount of energy produced.[26] Methane has a global warming potential (GWP) that is 72 times higher than that of CO_2 over 20 years and 25 times higher over 100 years, if no gas-aerosols interactions are taken into consideration.[27] Many studies that were completed with the objective of determining if natural gas, or shale gas, has in fact a lower impact on global warming compared to oil and coal, report contrasting conclusions.[28–33]

Table 1.5: Kilograms of combustion emissions of natural gas, coal and oil per billion BTU of energy produced (modified from EIA, 1999[26])

Air Pollutant	Natural gas	Oil	Coal
Carbon dioxide (CO_2)	53 100	74 400	94 300
Carbon monoxide (CO)	18	15	94
Nitrogen oxide (NO_x)	42	203	207
Sulfur dioxide (SO_2)	0.27	509	1 175
Particulates	3.18	38	1 245
Formaldehyde	0.34	0.10	0.10
Mercury (Hg)	0.000	0.003	0.007

A study by Jiang et al. (2011) showed that the life cycle GHG emissions of gas from the Marcellus shale is lower than coal for the production of electricity when effective carbon capture and storage are absent.[28] Another study by Burnham et al. (2012) found that the life cycle GHG emissions of shale gas were 6% lower than for conventional natural gas, 23% lower than for gasoline and 33% lower than for coal.[29]

However, Howarth et al. (2011) found that over a 20 years period, the GHG footprint of shale gas is 22 to 43% greater than that for conventional gases and 14 to 19% greater over 100 years. They also found that the GHG footprint of shale gas is at least 20% and 50% greater than that of coal and oil respectively over 20 years.[30] A modeling study by Wigley (2011) found that unless the methane leakage was kept under

2%, replacing coal with natural gas would not decrease the magnitude of future global warming.[31] Furthermore, Venkatesh et al. (2011) found that the use of natural gas instead of coal in power generation would have a high probability of decreasing GHG emissions[32] which confirmed findings by Jaramillo et al. (2007)[33] whereas if it were used for transportation its GHG emissions compared to diesel would probably be 10-35% higher.[32]

These studies show that there still are many controversies concerning the possible global warming effect of shale gas and the advantages/disadvantages on global warming of substituting coal and petroleum for natural gas. The discrepancy in the conclusions is partly due to differences in the estimations of full-life cycle methane emissions.[7] Further work is thus required to assess the global warming impacts of shale gas and to determine whether switching from oil and coal to unconventional gas would be more beneficial for the environment.

1.2.2.2   Fate of waste waters

A certain percentage of the 15.1 million liters of water used for each well[22] flows back to the surface within the first few weeks of drilling.[7] The exact percentage however is still unclear but has been reported to be as low as 8 to 15%,[34] and as high as 30 to 70%.[22] These flow-back waters not only contain the fracturing fluids (Table 1.4) but are also mixed with deep formation waters (or brines) that are found in or around the shale.[34] The formation water mixed with the injected water and the compounds that it contains are referred to as total dissolved solids (TDS).[35] These TDSs consist of organic matter, salts or minerals and their concentration can range from 0.8 to 300 g/L.[35] This

concentration is much higher than the usual TDS concentration in freshwater (0.1 to 0.5 g/L) or in the ocean (35 g/L).[35] The produced waters (flow-back waters and brine) constitute a very large volume (0.556 – 0.767 million liters for the average Marcellus well)[34] which, along with the high TDS concentration, is problematic when it comes to water treatment due to the difficulty of removing TDS from a very large volume of water.[23] The produced waters can also be contaminated with radionuclides such as radon, uranium or thorium, which is also a problem for wastewater treatment and waste disposal.[23]

Several techniques have been developed for the treatment of produced waters. They include mechanical vapour compression, which uses high quantities of energy to vaporize the water and separate it from the TDS, membrane distillation, which uses low grade heat to separate the water from its other constituents, and forward osmosis, which separates the water from the TDS using a membrane.[36] However these techniques are very costly mainly because they consume a lot of energy[36] and require the transport of the wastewaters to a treatment facility hence increasing the probability of spillage during transport.

Another mean of disposal is the discharge of produced waters to publicly owned treatment works (POTWs) for dilution with other wastewaters. However this disposal technique can also be problematic because of regulations governing wastewater treatment and high transport costs.[7,37] On-site re-use of the produced waters is difficult because of the high concentrations of TDS, which can precipitate and reduce gas production by blocking fractures.[37] The most common way to dispose of the produced

waters, however, is underground injection,[23,34,37] which also raises concerns because of the possibility of groundwater contamination.[23]

1.2.2.3 Water contamination (including possible health impacts)

An important concern linked to hydraulic fracturing is the potential of groundwater and surface water contamination. Rozell and Reaven (2012) recently evaluated the potential contamination risks associated with the main water contamination pathways: (i) leaks through well casings and (ii) fractured rocks, (iii) spills during transportation of wastewater, (iv) waste water disposal and (v) surface discharge. They found that wastewater disposal posed the highest contamination risk compared to the other pathways.[38]

Only a few cases of surface water contamination linked to hydraulic fracturing activities, including waste water disposal, have been reported. In 2008 however, the measured TDS concentration in the Monongahela River (PA, US) reached a maximum of 900 mg/L, much higher than the U.S. Environmental Protection Agency (EPA) limit of 500 mg/L.[39] Little is known about the fate and occurrence of chemicals used in hydraulic fracturing activities in groundwater and, unfortunately groundwater monitoring is rare.[40] Methane, the main component of shale gas is a smaller and more mobile molecule than the chemicals added to the fracturing fluids, can be a good tracer to determine potential groundwater contamination by hydraulic fracturing activities. This is an important issue since wastewaters produced by hydraulic fracturing contain chemicals that can have an impact on the health if ingested at a concentration higher than their toxicity level, with the most notable body targets being the sensory organs,

the respiratory, gastrointestinal and nervous systems, as well as the immune,

cardiovascular and endocrine systems.[24]

1.3 Source determination of methane

Methane is a small gaseous molecule and a potential asphyxiant. It is non-toxic

when inhaled but can become dangerous if present at high concentrations since it

reduces the relative concentration of oxygen in the air. It is also highly flammable at

concentrations in air of 5 to 15%.[41] Methane has 2 major sources: biogenic and

thermogenic.

1.3.1 Source identification

Four geochemical tools are typically used to determine the source of a gas:

molecular composition (hydrocarbon gases other than methane), carbon and hydrogen

stable isotope signatures (δ^{13}C and δD; see Appendix C for detailed explanation on

isotopic signatures) of methane and carbon isotopic signature of ethane and

propane.[42,43] Isotopic signatures of gases vary because of the isotopic signature of the

source material and the kinetic isotope effect (KIE) during the formation of methane and

higher hydrocarbon gases from the source material.[44] A primary KIE is observed when

the rates of a reaction during the rate determining step are different for a molecule

containing a light isotope compared to a heavy isotope. The primary KIE is only observed

for the isotopes involved in the reaction, as opposed to a secondary KIE which is

observed when an isotopic substitution occurs at a site not involved in the reaction.[45]

Because the reaction rate is lower for heavier compounds, a molecule containing the

heavier isotope reacts slower than the equivalent molecule containing the lighter

isotope.[45] Hence, the formed product is depleted in the heavy isotope compared to its

precursor. Fractionation during thermodynamic equilibrium can also lead to different

isotopic signatures of molecules containing a common element. During this equilibrium,

the heavier isotope will preferentially be incorporated in a compound in which it is

bound more strongly.[45] The KIE and the fractionation during thermodynamic equilibrium

lead to different isotopic compositions of compounds in nature. By analyzing the carbon

and/or hydrogen isotopic signatures of methane and higher hydrocarbon gases, it is

often possible to determine their source (i.e. biogenic or thermogenic).

1.3.2 Biogenic methane

Biogenic methane typically forms at shallow depths in anoxic environments. It is

produced by methanogenic bacteria that use carbonate or acetate as a carbon source.

$$\text{Acetate fermentation: } CH_3COOH \rightarrow CH_4 + CO_2$$

$$\text{Carbonate reduction: } CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \text{ (ref. 44)}$$
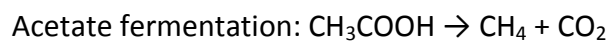
The acetate fermentation pathway involves the splitting and rearrangement of the

methyl and carboxyl group resulting in the formation of methane and carbon dioxide.[46]

In sulphate rich environments, methanogenesis is out-competed by sulphate reducing

bacteria. Methane formation by acetate fermentation is predominant in freshwater

sediments, which have characteristically low sulphate concentrations, whereas

formation by carbon dioxide reduction is prevalent in marine sediments where high

levels of sulphate result in a higher activity of sulphate reducing bacteria and hence a limited concentration of available acetate.[44]

Biogenic gases are almost entirely composed of methane but can contain traces of ethane.[47,48] Their gas wetness (defined as the ratio of methane concentration over the sum of the ethane + propane concentrations, or $C_1/(C_2+C_3)$) is typically >1000[43,49] and their methane carbon isotope signature ($\delta^{13}C$-CH_4) is usually between -110 and -50‰,[46] although a cut-off of -64‰ has been suggested in the absence of secondary processes such as bacterial oxidation. Hence a $\delta^{13}C$ lower than -64‰ is strongly indicative of a biogenic origin.[50] Typical δD of biogenic methane range from -400 to -150‰[44] but values as low as -531‰ have been measured.[51] When coupled with $\delta^{13}C$ analyses, the δD ratio can help identify the methane as biogenic as well as identify its formation pathway (i.e. carbonate reduction or acetate fermentation; Figure 1.2). If enough ethane is present in biogenic gases, its $\delta^{13}C$ ratio can also be used to classify the gas as biogenic. Taylor et al. (2000) reported $\delta^{13}C$ ratios for biogenic ethane from -73.9 to -45.4‰[47] although values as high as -35‰ have also been reported.[51]
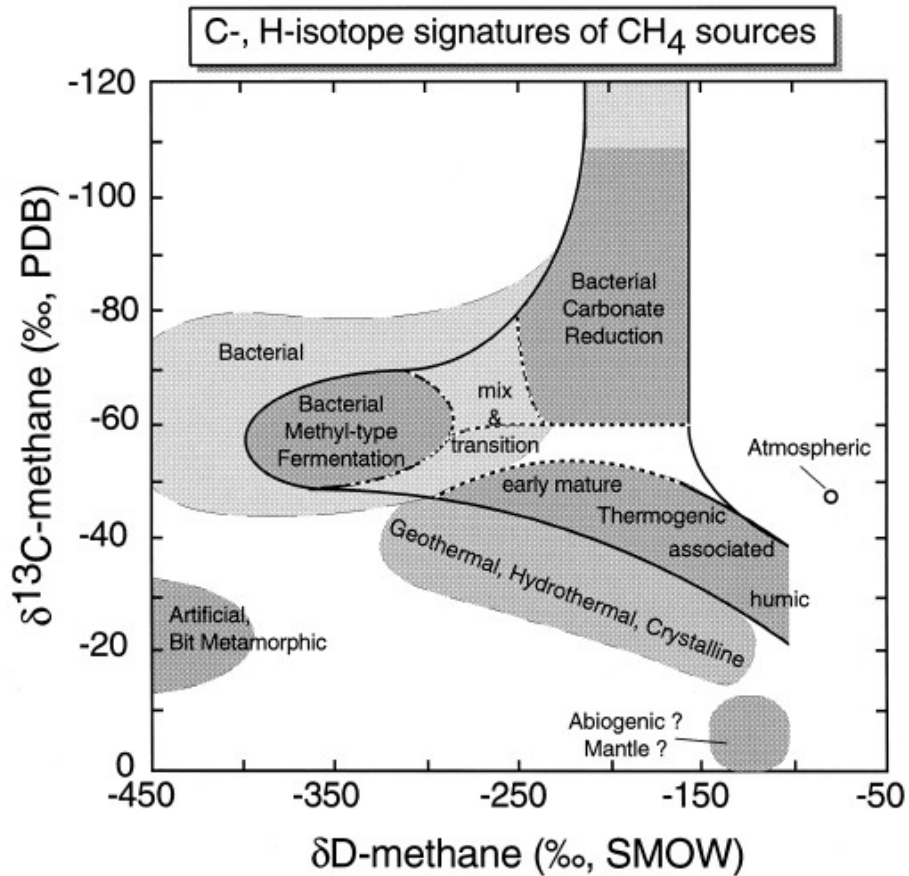
Figure 1.2: Source classification of methane based on $\delta^{13}C$ and δD isotopic signatures[44]

1.3.3 Thermogenic gas

Thermogenic methane forms at high pressure and temperature. It can be

associated with crude oils when it forms during or right after oil generation (petroleum

break down), or be produced later at higher thermal stresses (kerogen break down).[42]

Thermogenic gas typically has a $C_1/(C_2+C_3)$ below approximately 100 and are less

depleted in ^{13}C compared to biogenic gases, leading to $\delta^{13}C$ signatures higher than -

50‰.[49,50] A typical range for the δD of thermogenic methane is -275 to -100‰,[44]

although δD signatures as high as +124‰ have been reported.[52] Because of the overlap

between the δD signatures of thermogenic and biogenic methane, δD ratios can only

help to differentiate between the 2 sources if they are used in addition to $\delta^{13}C$ ratios.[44]

Because thermogenic gas generally contains a high enough concentration of

ethane allowing the measurement of its $\delta^{13}C$ ratios, this value can be used to determine

the source of the gas by combining it with other types of analyses. Taylor et al. (2000)

showed that by combining the δ^{13} of ethane and the $C_1/(C_2+C_3)$ ratio, one could

distinguish between thermogenic and biogenic gases where biogenic ethane would be

characterized by $\delta^{13}C$ signatures below -45‰ while the signature of thermogenic ethane

would be greater than -45‰.[47]

In most natural gases, the $\delta^{13}C$ of methane is lower than that of ethane, which is

lower than that of propane ($\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3$). However, field analyses and pyrolysis

experiments have shown that this trend is reversed ($\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3$) or partially

reversed for shale gas or gas forming from highly mature rocks, although the reasons for

this reversal are not fully understood.[53–58] Hence, taken together, the $\delta^{13}C$ of methane,

ethane and/or propane, the δD of methane and the $C_1/(C_2+C_3)$ ratio can be used not

only to differentiate between biogenic and thermogenic gas but can also to distinguish

shale gas from natural gas produced by less mature rock formations.

1.3.4 Migration, oxidation and mixing of hydrocarbon gases

Carbon isotopic and molecular compositions of gases do not only depend on the

source of the gas. Certain processes can alter the $\delta^{13}C$ of methane and the $C_1/(C_2+C_3)$

ratio. These processes include: mixing of thermogenic and biogenic gas, oxidation of

methane and migration of gas.[42,44,46,50,59,60] Mixing of gas from different sources results in changes in the $\delta^{13}C$ of methane and the $C_1/(C_2+C_3)$ ratio in proportion to the two end-member (thermogenic and biogenic).[42]

Methane can be oxidized to CO_2 in the presence of oxygen. Because of the KIE, $^{12}CH_4$ has a higher oxidation rate than $^{13}CH_4$, ethane and propane. This results in an enrichment in $^{13}CH_4$ in the remaining gas as well as in a decrease in the $C_1/(C_2+C_3)$ ratio.[42,44,46,60,61] In contrast, the migration of gas from deep sources through the bedrock does not result in significant isotope fractionation but leads to a higher $C_1/(C_2+C_3)$ ratio[42,60] since the smaller methane molecule migrates faster than ethane and propane. These processes must thus be taken into account when trying to determine the source of a gas.

1.3.5 Methane in ground water

Methane is a natural component of ground water. High concentrations of dissolved methane are found even in areas with no gas or oil drilling activities.[20,62,63] Because of the growing interest in shale gas and hydraulic fracturing, people are becoming increasingly concerned regarding the possible migration of methane from deeper sources. Several methane contamination pathways have been identified such as fugitive gas leakage from active and non active production wells or gas migration through natural and induced fractures.[40] An increasing number of studies have recently been published on methane concentrations and/or sources in ground water near hydraulically fractured wells.[64–69] However, only a few studies report methane

concentrations measured before hydraulic fracturing was initiated, to provide a baseline concentration to be used as a reference point in subsequent assessments of the impact of hydraulic fracturing on the quality of ground waters.[62,70] Despite the absence of natural, baseline concentration of methane in the ground waters of several areas that have been scrutinized, different conclusions have been drawn regarding contamination and the source of the methane dissolved in ground waters.

Osborn et al. (2011) and Jackson et al. (2013) found high dissolved methane concentrations in ground waters located within 1 km of Marcellus shale gas wells (PA, US). The stable carbon and hydrogen isotope signatures measured for the dissolved gases suggested a thermogenic origin.[65,66] In two other studies, Molofsky et al. (2011, 2013) concluded that the methane found in ground water in PA, US was more strongly correlated to topographic and hydrogeologic features than to shale gas activities.[68,69] In ground water of north-central Arkansas, Warner et al. (2013) found no relation between the concentration or source of methane and the distance to shale gas wells based on geochemical and methane isotopic analyses.[64] The absence of correlation between methane concentration and distance to oil/gas wells was also observed by Li and Carlson (2014) in north-eastern Colorado, although they observed a decrease in the number of wells with methane concentration > 5mg/L as the distance to an oil and gas well became greater than 700m.[67] Boyer et al. (2011) studied the water quality before and after drilling of Marcellus shale gas wells. They reported no statistical difference in dissolved methane concentrations in water wells before and after drilling was initiated except for one well in which the concentration of methane was higher after drilling.[70] A

study conducted by the USGS in 2012 assessed the natural concentration of methane in ground water from NY, US and found these concentrations could be up to 41 mg/L (exact number not specified in report).[62] To our knowledge, these are the only two studies that looked at the concentrations of methane in a large number of ground water wells prior to any hydraulic fracturing activities. There is thus a need for additional studies assessing ground water methane concentrations before and after drilling and fracturing the bedrock.

1.4   Scope of thesis

Because of the on-going controversy on the potential contamination of shallow ground waters during shale gas exploration and exploitation, it is important to assess the natural concentrations and sources of methane and higher hydrocarbon gases dissolved in water before the onset of drilling and hydraulic fracturing activities. Such natural baseline levels can then be used as a reference point in future studies in the area of interest and is the only way to determine with a high level of confidence the impact of shale gas exploration and exploitation on ground water quality. Furthermore, such studies would help identify areas where shale gas migration through natural cracks and faults in the bedrock leads to naturally high thermogenic methane concentrations in ground waters – areas that should not be exploited because of the increased risk of contamination.

The purpose of this project was thus to develop and optimize methods to precisely quantify the dissolved methane, ethane and propane concentrations in shallow ground

waters in 130 wells of the Lowlands of the St. Lawrence in Quebec, Canada, and to

determine their source by measuring the carbon isotopic signature of methane and

calculating the gas wetness ratio for each well.

2   Establishing baseline concentration and δ^{13}C signature of methane in shallow ground waters of the St. Lawrence Lowlands, QC, Canada: A tool for determining shale gas contamination

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2.1 Abstract

The use of hydraulic fracturing to recover hydrocarbons from unconventional sources such as shale gas is becoming an important drilling technique worldwide. In Quebec (Canada), the Utica Shale has been targeted by energy companies for future production. Public protest however lead to a moratorium on shale gas exploration and exploitation in 2010, and to a government-sponsored series of scientific, societal and economic studies on the risks and benefits of the exploitation of the resource in the future. As part of this effort, we determined the baseline concentrations and sources of naturally present methane in ground waters in Southeastern Quebec in the absence of fracturing activities, to be used as a reference in future assessment of potential groundwater contamination linked to hydraulic fracturing activities. Water samples were obtained from private (n=81), municipal (n=34) and observation (n=15) wells. Methane was detected in 80% of the wells with an average concentration of 3.81 ± 8.8 mg/L, and a range of < 0.0006 to 45.91 mg/L. The methane $\delta^{13}C$ of 19 samples was > -50‰, although further analyses only classified one sample as having methane from a thermogenic source, suggesting limited migration of gas from deep sources. The remaining samples for which $\delta^{13}C$ was determined seemed to contain gas from biogenic sources or gas that was subject to oxidation, migration or mixing. Localized pools of high concentrations of methane from predominantly biogenic sources were found throughout the study area.

2.2 Introduction

Interest in shale gas extraction has been increasing worldwide over the past decade.[71] In the US for instance, shale gas accounted for 23% of the total dry gas production in 2010, a proportion that is projected to increase to 49% by 2035.[15] Natural gas is "greener" than other fossil fuels and its combustion produces less carbon dioxide than coal or oil when the same amount of produced energy is considered.[23,72] For example, when combusted, natural gas produces 28% and 44% less carbon dioxide per unit of energy produced compared to the combustion of oil and coal respectively.[26] However these numbers do not consider the full life cycle of each fossil fuel, i.e. from extraction to combustion. Many studies looked at the atmospheric advantages/disadvantages of using unconventional gases instead of conventional ones and coal and oil, but the conclusions remain contradictory.[28–33] The extraction of shale gas utilizes a horizontal drilling technique referred to as hydraulic fracturing, or "fracking". This technique was developed to release the gas entrapped in pores by fracturing the shale rock to increase its permeability and hydraulic conductivity. This is done by pumping large amounts of water (>90% of total volume injected) mixed with fracturing fluids and proppant (usually sand) into the well at high pressure.[23,73]

The hydraulic fractures thus created and natural faults in the bedrock can lead to the migration of shale gas, fracturing fluids and deep formation waters to the atmosphere or to shallow aquifers.[40,65,69,74,75] How these migrations occur however is uncertain. The most probable pathways of ground water contamination by gas and fracturing fluids occur through migration along the well casing annulus, through

deficient storage or spillage of the flow-back waters or produced waters, which not only

contain fracturing fluids but are also contaminated with formation waters.[40,73] For

example, studies near the Marcellus shale gas extraction sites in the US have shown

high methane concentrations (up to 64 mg/L) in ground waters located within a distance

of 1 km from drilled wells. Carbon ($\delta^{13}C$) and hydrogen (δD) stable isotope analysis of

the gases suggested a thermogenic origin.[65,66] It is unclear, however, whether these

gases migrated through natural faults, drilling induced fractures or leaky casings.[65,66] On

the other hand, Li and Carlson (2014) found no correlation between the concentration

of methane and distance to gas/oil well or gas/oil well density in north-eastern

Colorado, although it appears that the number of wells with methane concentrations >

5 mg/L decreased as the distance to an oil or gas well became greater than 700 m.[67]

Another study linked the presence of methane in ground waters to the altitude of the

wells, with lowland water wells characterized by higher methane concentrations than

those located in upland areas.[69] A further study published by the USGS in 2012 reported

natural concentrations of methane in NY ground water but did not assess its source.[62]

To our knowledge, only one study reported the analysis of ground water quality before

and after drilling activities were initiated.[70] Boyer et al. (2011) reported no statistical

difference in dissolved methane concentrations in the majority of ground water wells

before and after drilling and found only one well in which the concentration of methane

was higher after drilling.[70] However, their study was limited in time (post-drilling

sampling occurred within 8 months after hydraulic fracturing) and methane

contamination episodes might have been missed. Monitoring over longer periods is

necessary to determine potential contamination owing to the slow migration rate of contaminants (gas and fluid) through the well casing and the bedrock.[76]

To assess whether contamination is associated with hydraulic fracturing, it is therefore important to monitor the baseline concentrations and sources of hydrocarbon gases, and methane in particular, prior to shale gas extraction,[40,65,66,77] as light hydrocarbons from deep thermogenic or shallow bacterial sources occur naturally in shallow ground waters.[70,78–80] To differentiate between sources, and to understand the effect of processes such as migration of gases through the bedrock, their oxidation to CO_2 and the mixing of different sources,[42,44,46,50,59,60] stable carbon isotope signatures must also be determined in parallel to concentration measurements.

In south-western Quebec (Canada), the Utica Shale has been targeted by energy companies because of its potential for shale gas production, which still has to be fully assessed.[12] The provincial government however has decreed a moratorium in 2011 and launched a strategic environmental assessment to gather information on the potential economical, sociological and environmental impacts of shale gas exploration and exploitation in the province.[19] This present study was carried out as part of the assessment and thus took advantage of the unique opportunity to measure light hydrocarbon concentrations and $\delta^{13}C$ signatures in shallow ground waters in an area not affected by natural gas exploitation, and hence to document the natural, or baseline, concentrations and sources of these dissolved gases.[20] Over a period of 10 months (August 2012 to May 2013), water from 130 municipal, private and observation wells were sampled and characterized for a range of parameters, including light hydrocarbons

(this study). With the results presented here and a thorough assessment of temporal and spatial variability of gas concentrations and sources, the potential impact of shale gas exploitation on ground water quality will be better understood.

2.3 Materials and methods

2.3.1 Geographical settings

Located in the St. Lawrence Lowlands (Quebec, Canada, Figure 2.1), the study area covers approximately 14 000 km² between Montreal (south-west) and Quebec City (north-east), the Appalachians mountains (south-east) and the St. Lawrence River (north-west). The sampled wells are located in the Bécancour, Montérégie and Nicolet-Saint-François regions, as well as around the city of Trois-Rivières on the north shore of the St. Lawrence River. Ground waters in these regions are being extensively characterized as part of the provincial initiative PACES (*Programme d'acquisition de connaissances sur les eaux souterraines*).[81–84] As of 2010, a total of 27 gas wells had been drilled for gas exploration in the Utica shale, 18 of which had been hydraulically fractured.[12] These wells have only been fractured on a small scale for exploration purposes before 2010.

2.3.2 Geology and hydrogeology

Figure 2.1 shows the distribution of the major geological areas and structural elements of the study area. The geological sequence of the region consists of: 1) the Precambrian Grenville Province with igneous and metamorphic rocks outcroping north

of the St. Lawrence River, 2) the St. Lawrence Platform of sedimentary origin from the

Cambrian and Ordovician, 3) the Appalachian mountains where the rocks are of

sedimentary origin from the Cambrian and Ordovician, and 4) the Monteregian hills,

consisting of igneous intrusions from the Cretaceous.[85] The majority of the sampled

wells are located in the St. Lawrence Lowlands, which from bottom to top consist of the

Postdam Group from the Middle-Upper Cambrian, the Beekmantown from the Lower-

Middle Ordovician and the Chazy, Black River, Trenton, Utica, Lorraine and Queenston

from the Middle-Upper Ordovician. The Utica Shale is composed of calcareous black

mudstone and has a thickness of 30 to 300 m.[10] It is overlain by the thick Lorraine

Group, composed of sandstones and siltstones.[86] The Queenston Formation is found at

the top and consists of shale, sandstone, siltstone and limestone.[86] The study area is

marked by multiple faults, with the most important ones being the Yamaska fault and

the Logan line that separates the St. Lawrence Lowlands and the Appalachians.
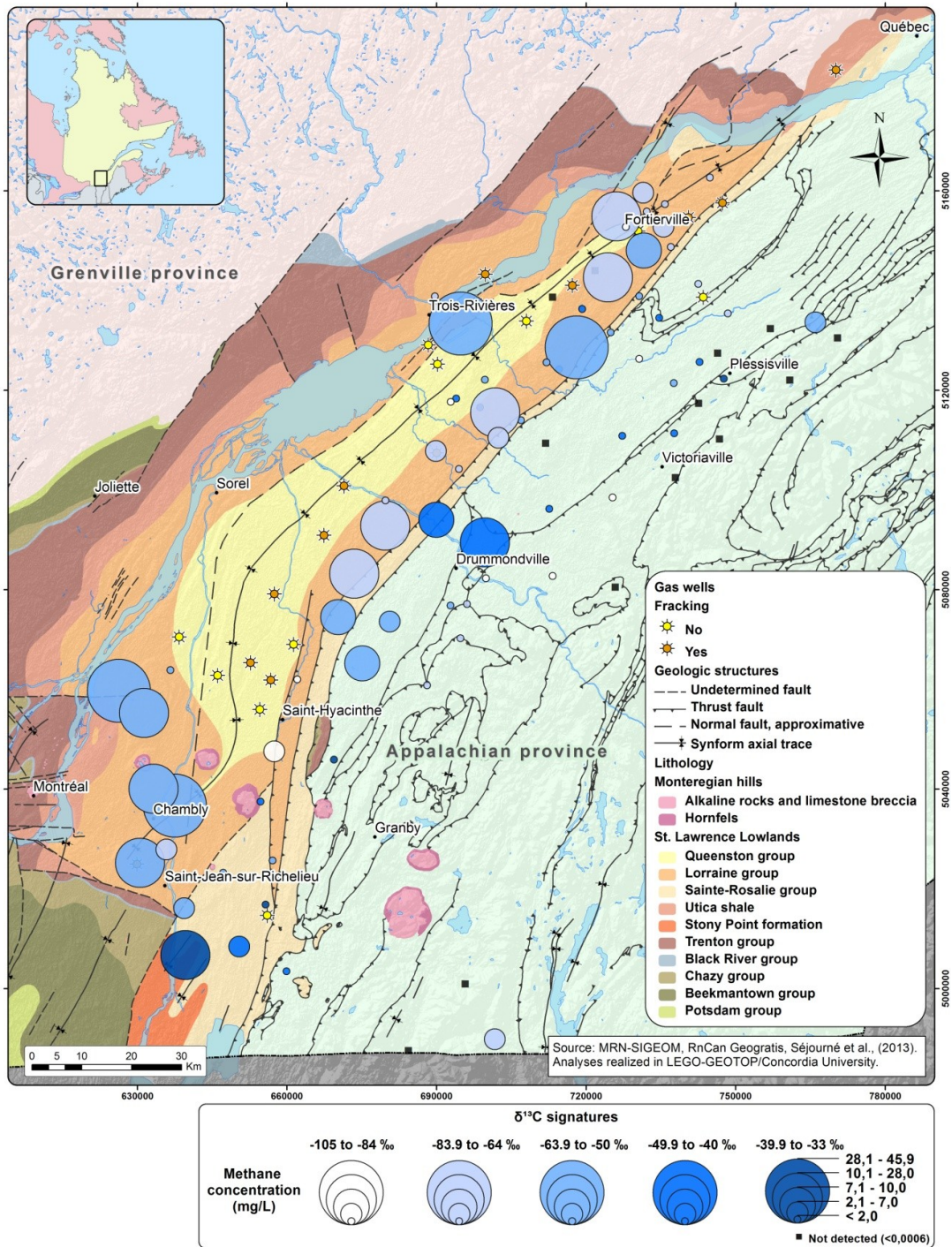
Figure 2.1: Map of sampled area and the St Lawrence Lowlands geology and geologic structures. Methane concentrations are represented with the size of the circles and methane δ¹³C signatures by their colour

2.3.3 Sampling and analysis

Sampling. Water samples were collected throughout the St Lawrence Lowlands (Figure 2.1). A total of 130 sites were visited on private properties (n=81), municipalities (n=34), as well as observation wells (n=15) that are not used for human consumption. The wells were extensively purged to remove water from pipes and stagnant water, which may have degassed. Temperature, conductivity and pH were monitored for each well and the water was sampled only once the values remained stable (at least 3 consecutive measurements within 15 minutes). Water was sampled as close to the well as possible, prior to any water treatment or filtration, into 60-mL glass bottles by inserting a Tygon® tube into the bottle and immerging the bottle upside down into a bucket filled with constantly flowing water. The water filled the bottle slowly as the air in the bottle was displaced through the tube. This sampling method insured that air bubbles were purged from the bottle and that the sample water did not degas. Once the bottle was filled, the tube was removed and 1 mL of 6N HCl was added to the bottle while still submerged in the water bucket. The bottle was then sealed with a 20-mm Teflon lined crimp cap while under water. The samples were then kept at 4°C until analysis. Laboratory measurement on a series of bottles collected on the same day from the same site revealed that the samples could be stored for as many as 83 days without significant variation in the dissolved gas concentration (Appendix B).

Analysis. A modified version of the method of Kampbell & Vandegrift (1998) was used to extract the gases from the water samples.[87] On the day of the analysis, once the

bottles had equilibrated with the temperature of the laboratory, a headspace was created by displacing 10% of the bottle volume (6 mL) with ultrapure helium (He). Two stainless steel needles were inserted through the septum of the bottle, the first one connected to the He tank through a Teflon tube and the second one directly attached to a syringe. He was then allowed into the bottle at a rate of less than 5mL/min, displacing the water out of the bottle and into the syringe. The needle connected to the He tank was removed once 10% of the total volume of water had been displaced, followed by the removal of the second needle attached to the syringe. The samples were then shaken gently for 10 minutes to reach equilibrium between the liquid and gas phases. The mass of the sample was recorded before and after creating the headspace to insure that the exact headspace volume was used in the dissolved gases concentration calculations. Exactly 500 μL of the headspace was then injected manually onto an Agilent 6890N gas chromatograph equipped with a flame ionization detector (GC-FID) and a Rt-QPLOT capillary column (Restek) to determine the dissolved hydrocarbon concentrations. The splitless injection mode and a constant column flow rate of 30 mL/min were used. The injector and the detector were kept at a constant temperature of 120°C and 200°C, respectively. The oven was held at the initial temperature of 60°C for 2 min and then ramped to 120°C at 60°C/min. This final temperature was held for 2 min.

The sample concentrations were determined using calibrated in-house standard gases (methane, ethane and propane). The isotopic signatures of the gas standards were determined beforehand and were normalized on the NBS19-LSVEC scale ($\delta^{13}C$ =

1.95‰ and $\delta^{13}C$ = -46.6‰ respectively[88]). For calibration purposes, the conversion of the hydrocarbons to CO_2 was performed offline using cupric and nickel oxide combustion under vacuum.

To determine the carbon isotope signatures of the dissolved hydrocarbons, the sample headspace was injected manually onto an Agilent 6890N GC coupled to a combustion interface and an Isoprime (Elementar Americas Inc.) isotope ratio mass spectrometer (GC-C-IRMS). Because of partial CO_2 and CH_4 co-elution issues for samples with a high CO_2 concentration, about 500 mg of Carbo-Sorb® was added to the quartz inlet of the GC injector to remove carbon dioxide from the injected sample. The Carbo-Sorb® was renewed at the beginning of each day of analysis. It did not remove any CH_4 from the samples and had no effect on the measured $\delta^{13}C$ signatures of CH_4. The column flow rate was kept constant at 1.5 mL/min and the oven temperature remained at 30°C to insure baseline separation between the different gases. The temperature was raised to 200°C for 15 min after each day of analyses to remove any potential contaminant with a boiling higher than 30°C from the column. The quartz tube of the combustion interface was filled with platinum wire (catalyst) and a mixture of 30% cupric and 70% nickel oxides (0.5 mm particle size). The combustion interface was kept at 950°C throughout the analyses.

The overall precision of the GC-FID and GC-C-IRMS methods were determined as was 6.24% and 0.91‰, respectively by injecting 5 samples collected on the same day from the same site. The limits of detection (3σ) and quantification (10σ) are reported in Table 2.1. To determine the hydrocarbon concentration, each sample was analyzed in

34

duplicate with 2 injections per duplicate (total of four injections). The minimum concentration of methane needed for $\delta^{13}C$ analysis on the GC-C-IRMS was 0.03 mg/L (Table 2.1). The concentrations of ethane and propane in the samples were too low to measure their $\delta^{13}C$ signature.

Table 2.1: Average, median, range of methane, ethane and propane concentrations (in mg/L), and methane $\delta^{13}C$ signatures (in ‰). The experimental detection/quantification limits are also provided

	Methane (mg/L)	Ethane (mg/L)	Propane (mg/L)	Methane $\delta^{13}C$ (‰)
Average	3.8 ± 8.8	0.010 ± 0.018	0.003 ± 0.002	-62.3
Median	0.1	0.003	0.002	-60.0
Maximum	45.9 ± 0.8	0.086 ± 0.003	0.006 ± 0.004	-24.8
Minimum	< 0.0006	< 0.0004	< 0.0010	-105.1
Limit of detection[a]	0.0006	0.0004	0.0010	N/A
Limit of quantification[b]	0.0020	0.0010	0.0030	N/A

[a] 3 standard deviations

[b] 10 standard deviations

2.4 Results and discussion

Determination of light hydrocarbon gas concentrations. Dissolved methane was detected in 117 of the 130 wells. The average methane concentration was 3.8 ± 8.8 mg/L, the median was 0.1 mg/L, and the range was < 0.0006 to 45.9 mg/L (Table 2.1). In 84 samples with detectable methane levels, the measured concentrations remained low, below 1 mg/L (Figure 2.2). The concentrations of ethane and propane were detectable in only 42 and 10 wells, respectively, with concentrations below 0.086 and 0.006 mg/L, respectively (Table 2.1).

In May 2013 the *Ministère du Développement durable de l'Environnement, de la Faune et des Parcs* of Quebec approved a series of regulations for the protection of ground waters in Quebec and set the maximum allowable concentration of methane in ground water at 7 mg/L.[89] At a total of 18 stations, the concentration exceeded 7 mg/L, averaging 21.8 ± 11.0 mg/L (Figure 2.2). At 4 of these 18 stations, methane concentrations were higher than 28 mg/L, which corresponds to the solubility of methane in water at 1 atm and 15°C. Finding such high concentrations can be problematic since they indicate that methane is spontaneously degassing and can thus, potentially, accumulate in closed, unventilated areas.

Only a few studies reported natural concentrations of methane in ground water. Our data is in agreement with the methane concentrations measured by the USGS (2012) on ground water in the State of New York (US). Their study revealed that 2% of the samples collected (n=239) had methane concentrations higher than 28 mg/L

(compared to 3% in our study), with the maximum concentration around 41 mg/L (exact

number not provided).[62] Their analysis however, did not include the $\delta^{13}C$ signatures of
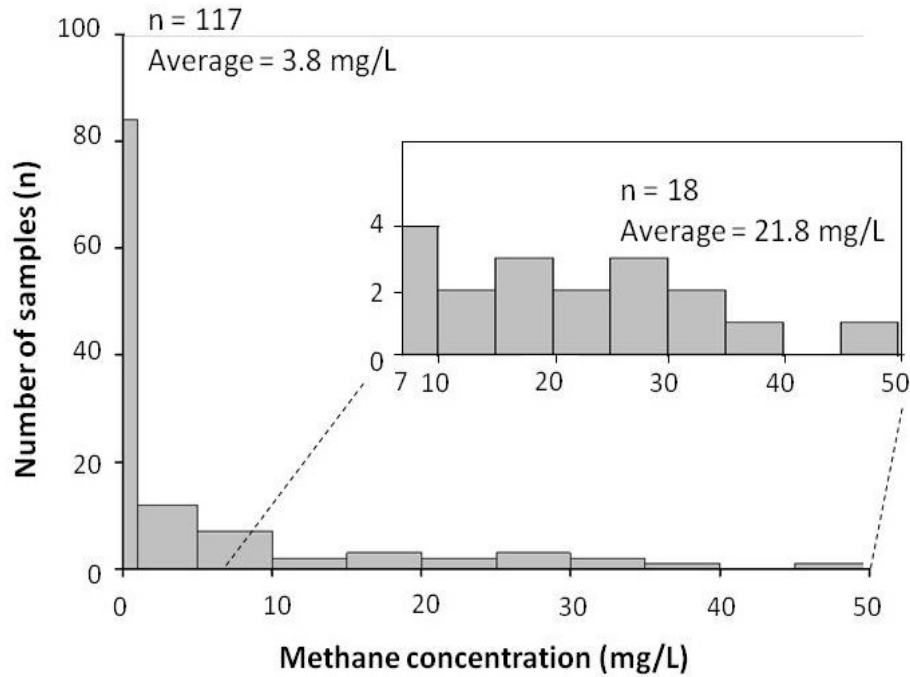
methane.

Figure 2.2: Distribution of methane concentrations from 0 to 50 mg/L and from 7 to 50

mg/L (insert) for samples with detectable CH_4 concentrations

Source determination of methane using $\delta^{13}C$ isotopic signatures. The $\delta^{13}C$ signature of

methane was determined for 73 samples, with isotopic signatures ranging from -105.1

to -24.8 ‰. $\delta^{13}C$ signatures of methane below -64‰ are usually indicative of a biogenic

source if minimal methane oxidation occurred,[50] although less depleted $\delta^{13}C$ values are

also possible depending on the methane precursor.[44,46] For instance, methane

produced in freshwater sediments show $\delta^{13}C$ ranging from -65 to -50‰.[46] In contrast, methane $\delta^{13}C$ signatures ranging between -50 and -20‰ suggest a thermogenic source,[44] although slightly more ^{13}C-depleted values have also been observed.[50]

In this work, $\delta^{13}C$ values lower than -64‰ were used to indicate a predominantly biogenic origin and $\delta^{13}C$ signatures higher than -50‰ a predominantly thermogenic origin. Out of the 73 samples with CH_4 concentrations greater than 1 mg/L, 31 had $\delta^{13}C$ signatures more depleted than -64 ‰, while 19 others had $\delta^{13}C$ signatures less depleted than -50 ‰ (Figure 2.3). The majority of samples with a less depleted $\delta^{13}C$ signature were characterized by low methane concentrations (<1 mg/L). Of these 19 samples with a $\delta^{13}C$ signature > -50 ‰, 3 had methane concentrations > 7 mg/L, with one sample having a concentration of 26.4 ± 1.9 mg/L, close to the solubility of methane at 1 atm and 15°C (28 mg/L). For samples with a $\delta^{13}C$ signature < -64 ‰, 5 showed methane concentrations > 7 mg/L, and one as high as 27.8 ± 3.4 mg/L. The vast majority of samples with methane concentrations above 7 mg/L (n = 18) showed isotopic signatures between -64 and -50 ‰ (n = 10 of 18), with a maximum concentration of 45.9 ± 0.8 mg/L (Figure 2.3).
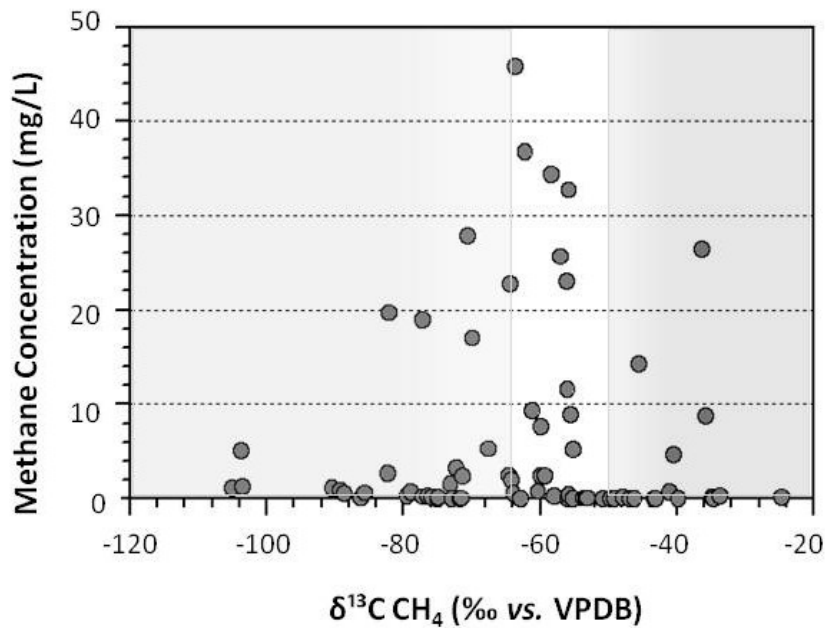
Figure 2.3: Relationship between methane concentrations and δ^{13}C signatures. Grey areas depict the delimitations between biogenic (left grey area) and thermogenic (right grey area) methane

Source determination of methane using gas wetness and processes affecting source identification. Thermogenic gases normally contain higher concentrations of ethane, propane and other higher hydrocarbon gases compared to biogenic gases.[50] The concentration ratios between methane and the sum of these higher hydrocarbon gases ($C_1/(C_2+C_3)$), also referred to as gas wetness, can be used as a source indicator. Ratios greater than 1000 indicate a biogenic source while ratios lower than 100 indicate a thermogenic source.[42,44,50,59,60] Figure 2.4 shows the ratio $C_1/(C_2+C_3)$ plotted against the δ^{13}C signature of methane for samples with concentrations that allowed measuring

these parameters. This graphical representation shows that the majority of the samples

plot outside the thermogenic gas window. The only sample falling within the

thermogenic window had a low methane concentration (0.4 ± 0.004 mg/L). Thus, none

of the samples with high methane concentrations (> 7mg/L) and less depleted in ^{13}C

(δ^{13}C > -50‰) appears to be of thermogenic origin.

However three processes can alter the gas wetness and/or the δ^{13}C signature of

methane: 1) mixing of different sources, 2) oxidation of methane and 3) migration or

diffusion of gas.[42,44,46,50,59,60] The mixing of gases can be represented on Figure 2.4 by a

multitude of mixing curves that vary according to the gas wetness ratio and the δ^{13}C

signature of the end-members. Two such theoretical mixing curves are represented in

Figure 2.4 with different thermogenic and biogenic end-members.

Oxidation of methane takes place in oxic environments at shallow depths and

results in an enrichment in ^{13}C of the residual methane, as well as in a decrease in the

$C_1/(C_2+C_3)$ ratio[42,44,46,60,61] since the oxidation kinetics of $^{12}CH_4$ are higher than those of

$^{13}CH_4$, and the oxidation kinetics of methane are higher than those of ethane and

propane.[44] On the other hand, the migration of gas results in a higher $C_1/(C_2+C_3)$ ratio

since the diffusion rate through the bedrock is higher for methane compared to ethane

and propane, but it is generally accepted that it does not affect the δ^{13}C signature of

methane to a significant extent.[42,60]

The samples from Figure 2.4 that plot outside of the biogenic or thermogenic window

could have been affected by one of more of these processes (i.e. mixing, oxidation and

migration). For example, three wells showed high concentrations of methane with a δ^{13}C

> -50‰ (Figure 2.3) although their $C_1/(C_2+C_3)$ ratio was > 100 (Figure 2.4), suggesting an alteration of the original gas composition. The present data is however insufficient to draw conclusions on the processes taking place for each one of these samples. Furthermore, the methane from samples falling within the thermogenic and biogenic window could also have been subjected to these processes to some extent, even though their $\delta^{13}C$ and $C_1/(C_2+C_3)$ ratio indicate a thermogenic or a biogenic origin. More analyses, such as the determination of the $\delta^{13}C$ signature of ethane and/or the δD signature of methane, are thus required to determine the exact processes that affected the gas wetness or $\delta^{13}C$ signature of methane in these samples.
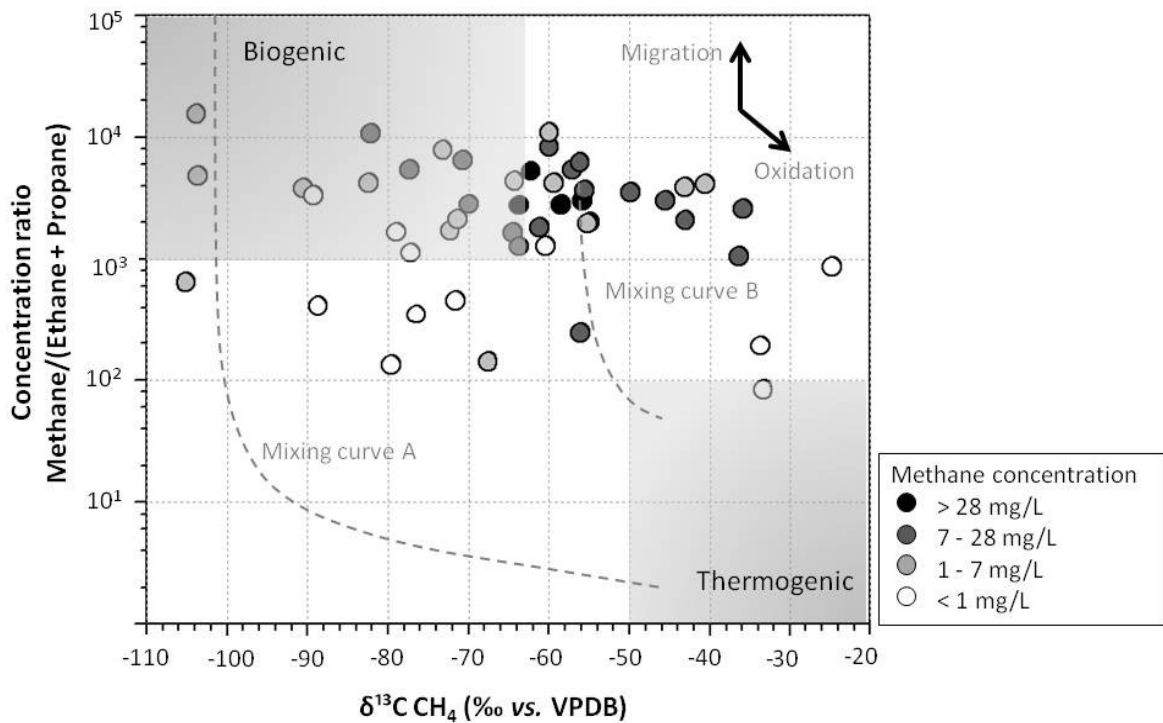
Figure 2.4: Bernard plot of methane / (ethane + propane) ratio versus $\delta^{13}C$ of methane

for the samples analyzed in this study. Grey areas depict approximate delimitations for

biogenic and thermogenic methane. Mixing curves A and B are theoretical mixing curves

modified from Whiticar.[44] The arrows indicate the general direction of the methane /

(ethane + propane) ratios and the $\delta^{13}C$ of methane upon oxidation or migration.

Modified from ref. 49 and 43.

Geographical distribution of methane. The highest concentrations of methane were

found along the Yamaska, Logan and d'Aston faults on the south shore opposite to

Trois-Rivières, around the city of Chambly and north-east of Montreal (Figure 2.1).

Dissolved methane concentrations in these areas were approximately 10 times higher

than the average groundwater methane concentrations in the St. Lawrence Lowlands. The Logan line, which corresponds to the boundary between the St. Lawrence Lowlands and the Appalachians, is a clear tipping point between high and low dissolved methane concentrations.

The mapping of concentrations and sources of methane shows that the majority of wells with high methane concentrations fall within the Lorraine formation (Figure 2.1). It is possible that the gas in these samples came from upper layers of the Lorraine Group where methane would be more depleted in ^{13}C compared to methane from deeper layers. This gas could have migrated through natural faults in the area and dissolved in ground water where it could have been mixed with biogenic gas already present in the water.

Possible temporal variations of the concentrations and δ^{13}C signatures of methane. The majority of our samples were collected over a period of 4 months between August and November 2012 (hereafter labeled summer and fall 2012, respectively), but 22 samples were collected in April/May 2013 (spring 2013) to improve our spatial coverage in areas with a low well density (14 new wells) and to test for temporal variability in methane concentrations and δ^{13}C signatures (8 wells already sampled in summer and fall 2012).

Among the re-sampled wells, all 4 samples collected in the summer of 2012 had methane concentrations that were significantly different than the ones measured in the spring of 2013 samples ($p < 0.02$), although the concentrations for 2 of these samples

remained below 1 mg/L in both cases (Figure 2.5). Only one sample (sample 3) collected

in the summer of 2012 had a methane δ^{13}C signature that was significantly less depleted

in ^{13}C compared to the spring 2013 sample (Figure 2.5; p = 0.0022); all other summer

2012 samples had methane δ^{13}C signatures that were not significantly different to the

samples collected in the spring of 2013.

The samples collected in the fall of 2012 all had similar methane concentrations

when re-sampled in the spring of 2013 (p > 0.37), except for sample 5 for which the

methane concentration remained low (< 1 mg/L) but significantly different (p < 0.0001)

(Figure 2.5). Methane from 3 samples collected in the fall of 2012 showed significantly

less depleted δ^{13}C values compared to the spring 2013 samples (p < 0.0001), while the

opposite trend was observed for sample 7. Overall however, the δ^{13}C signatures of

dissolved methane appear to be less depleted in ^{13}C in the summer and fall compared to

the spring.
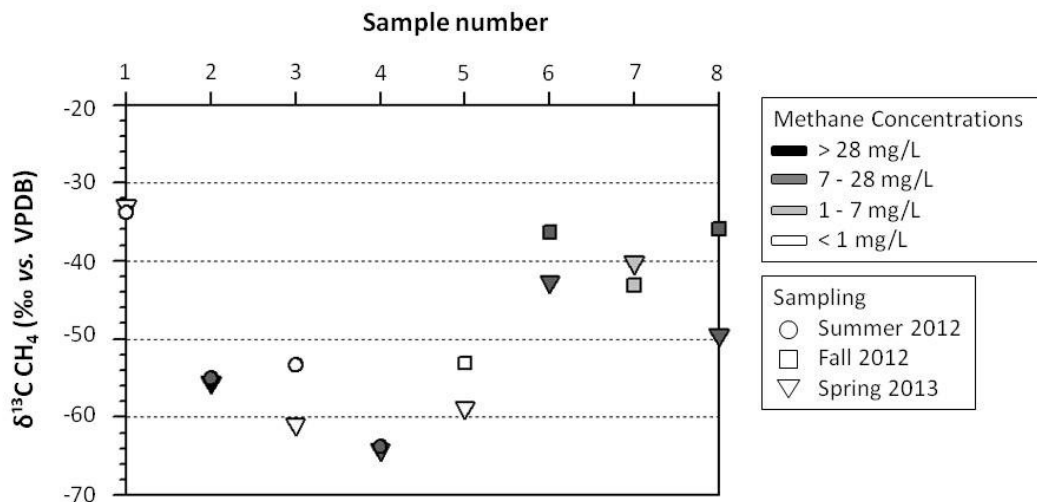
Figure 2.5: Distribution of methane concentrations and δ^{13}C for 8 samples collected

during different seasons (standard deviation < 1‰).

Several studies have shown that the $\delta^{13}C$ of methane in water is shifted toward higher values during the warmer months of the year,[90–92] either because of a change in substrate (e.g., a predominance of sulfate fermentation compared to carbonate reduction[91,92]), or to an increase in atmospheric oxygen penetration into the water due to the lower water levels in summer, which would lead to methane oxidation.[90] Because of these potential seasonal variations, further studies are necessary to better understand how seasonal variations could affect the concentration and $\delta^{13}C$ of gases dissolved in ground water and the processes that cause these variations.

Conclusions. This study showed that methane is a natural component of ground waters from the St. Lawrence Lowlands and can be present at concentrations that surpass solubility under conditions encountered in the wells. $\delta^{13}C$ measurements suggest that methane found in these ground waters is mostly produced by methanogenic bacteria, although the gas composition may have been altered by processes such as the mixing of deep thermogenic and shallow biogenic sources, bacterial oxidation of hydrocarbon gases, or migration of deep gases. Additional analyses, such as the $\delta^{13}C$ signature of ethane and propane as well as δD of methane, are required to pinpoint the exact sources of this gas and the processes that may have altered it.

The present study addressed an important need by providing natural methane, ethane and propane concentration levels in ground waters throughout an area that is targeted by energy companies for shale gas exploitation. To our knowledge, it is the first study in Canada designed to assess these baselines before hydraulic fracturing takes

place. These baseline concentration levels will be used as a reference in future studies on the potential impact of shale gas extraction on the quality of shallow ground waters if or when the moratorium is lifted.

Acknowledgments

3   General conclusion

Our study, the first of its kind in Canada, allowed determining the natural concentrations of methane, ethane and propane dissolved in ground waters throughout the St. Lawrence Lowlands where shale gas exploitation could take place in the future. It filled the need for getting a clear picture of the natural, baseline concentration of methane in ground waters, which is essential to better understand if a contamination event occurred and to link the event to specific industrial activities. Our study showed that methane is a natural component of ground water in Quebec and that methane concentrations can exceed the maximum allowable level of 7 mg/L. Our work was also socially relevant as it allowed identifying wells that should be closely monitored (CH_4 level > 7 mg/L) or immediately vented (CH_4 level > 28 mg/L, corresponding to the solubility of methane under these conditions) to avoid methane build-up in closed areas and reduce explosion risks.

In addition to these benefits, the analysis of the $\delta^{13}C$ signature of methane showed that methanogenic bacteria are responsible for most of the methane found in these shallow ground waters and that little migration from deep thermogenic sources occurred. Because methanogenic bacteria produce very little to no ethane[47] and no propane, their concentrations were very low in the ground waters studied here, which did not allow the measurement of their $\delta^{13}C$ signatures. Much larger, and hence unpractical volumes of water would have been needed to measure the $\delta^{13}C$ signatures of ethane and propane, which can not only help differentiate biogenic from

thermogenic gas but can also distinguish shale gas from conventional thermogenic gas because of the unique reversal in $\delta^{13}C$ signatures in the former (i.e., $\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3$).[53–58] In addition to the $\delta^{13}C$ signatures of methane, ethane and propane and the gas wetness, the δD signature of methane can also be exploited to assess the source of the gas. Ideally, these parameters should all be measured in parallel to improve the identification of the sources of hydrocarbon gases dissolved in shallow ground waters. Unfortunately, this could not be done in this study because of time and monetary constraints. Furthermore, a thorough knowledge of the geology and hydrogeology of the study area is required to establish the possible contamination pathways from deep thermogenic sources and shallow biogenic sources.

It is debated whether hydraulic fracturing activities can lead to methane leaks into ground waters, what the main pathways are and how severe this contamination can be. This study is the first of several steps required to better understand how these leaks occur, how long it would take for the methane to migrate from deep sources and how much methane actually reaches the shallow aquifers. More analyses in time and space, and with a more complete set of measured parameters, should thus be carried out in the future. In particular, the same ground water analyses should be repeated at varying time intervals if shale gas extraction is initiated since methane can take years to migrate into shallow ground waters;[76] it is a good marker for detecting contamination by fracturing fluid leaks, which can be extremely toxic.

Our study only assessed an environmental aspect: potential contamination of shallow ground waters by hydrocarbon gases and, possibly, fracturing fluids. It is

however important to note that hydraulic fracturing activities do not only pose potential threats to the quality of ground waters and the atmosphere, but also affect the quality of life and the health of individuals living in the areas targeted by oil and gas industries. The Utica shale is overlain by one of the most densely populated areas in Quebec with more than 3 million inhabitants, an area that at the same time harbours the best agricultural soils in the province. The construction and functioning of hydraulic fracturing industries increase the noise, air pollution, and traffic; they also generate immense volumes of highly contaminated wastewaters that have to be treated, most often at distant locations. Furthermore, it requires more housing for workers, affects wildlife and scenery, decreases the values of the properties, and perturbs the general quality of living and peace of mind of inhabitants who often have chosen to live away from large urban centers to distance themselves from these nuisances. The questions we need to ask ourselves are: How will shale gas development affect the local Quebec population? Does shale gas exploitation really answer our energy needs? Shouldn't we shift our focus to more sustainable energies?

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Appendix A: GC-C-IRMS optimization tests

The GC-C-IRMS method implementation consisted of various tests and optimizations. One issue encountered during the optimization of the method was a poor separation of the methane and carbon dioxide peaks that affected the measurements of the methane $\delta^{13}C$ signatures (Figure A.1). The resolution of these peaks was not improved by altering the column temperature and the helium flow rate. Therefore, a small amount of Carbo-Sorb® was added to a glass inlet in the injector. This addition resulted in the removal of CO_2 from the sample. The Carbo-Sorb® was changed after each day of analyses to avoid break-through of CO_2.

Another test performed on the GC-C-IRMS was the measurement of a methane, ethane and propane mixture with closed and open split (Figure A.2). The results show a better separation of these three gases, and sharper peaks when the split was opened. Also a closed split resulted in a pressure built-up in the system which lead to the shut down of the source of the IRMS. The open split allowed the injection of the high volumes (500 µL) required for samples with low concentrations of methane.

Finally, the temperature of the column and the helium flow rate were also optimized. At a temperature of 60°C and a helium flow rate of 1.8 mL/min, the resolution between the peaks of methane and carbon monoxide was poor (Figure A.3), which affected the accuracy of the $\delta^{13}C$ measurement of methane. To improve resolution, the column temperature was maintained at 30°C throughout the run and the helium flow rate was decreased to 1.5 mL/min. In addition, because this low column

temperature can result in water buildup in the column, hence affecting the separation

and resulting in column degradation, a bakeout at 200°C for 30 min was performed at

the end of each day of analyses.
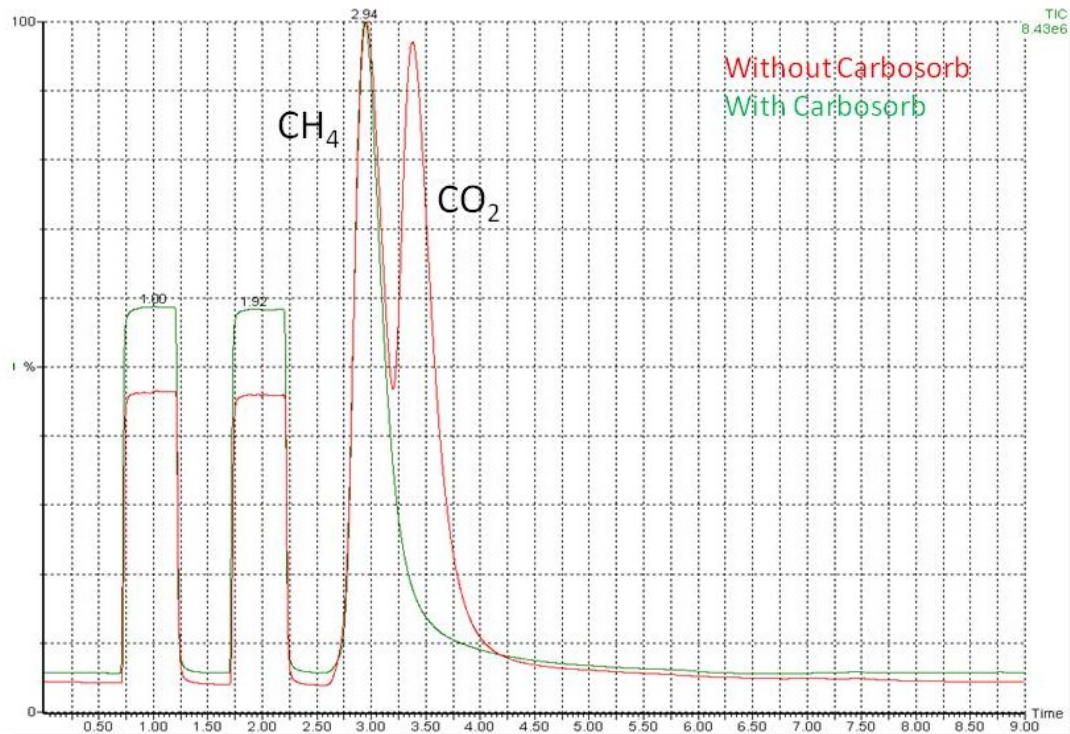
Figure A.1: GC-C-IRMS of a CH_4 and CO_2 containing sample with (green trace) and

without (red trace) carbosorb. The first two flat peaks correspond to the calibrating

reference gas
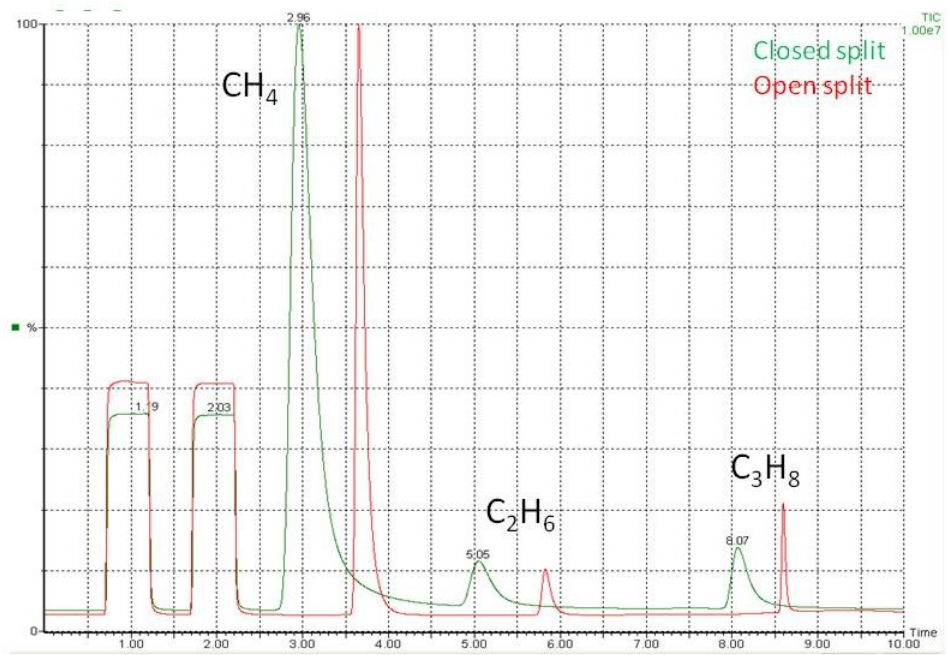
Figure A.2: GC-C-IRMS separation with an open (red) and closed (green) split

| Column temperature | 60°C | 30°C |
| He flow rate | 1.8 mL/min | 1.5 mL/min |
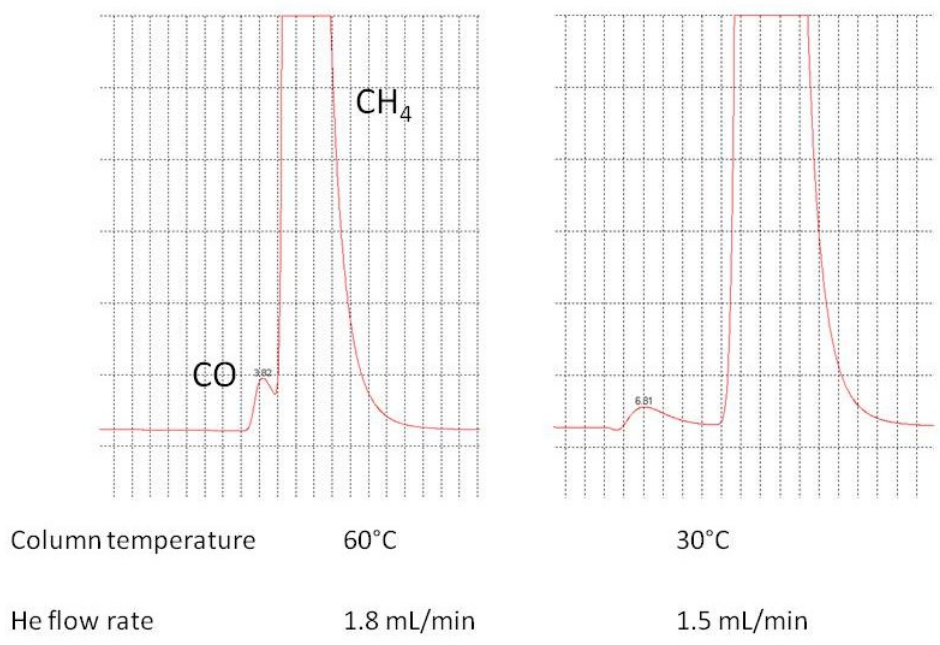
Figure A.3: GC-C-IRMS separation of the carbon monoxide and methane peaks under

varying oven temperatures and helium flow rate

Appendix B: Sample preservation

We also tested the effect of preservation time on the quality of the results. Eight samples were collected from the same well and were analyzed at regular intervals over a period of 118 days (Figure B.1). The measured concentration remained similar throughout the experiment, with no significant difference compared to the first measurement ($p > 0.3$). Even though this test shows that the samples can be preserved for as long as 118 days before analysis, standard deviations started to increase for samples kept longer than 83 days. All our samples were analyzed within three weeks of collection. The $\delta^{13}C$ signature of this same sample was measured on day 0 and day 14 and the difference between those measurements was within the expected experimental error (0.91‰). Although no GC-C-IRMS analyses could not be done past 14 days owing to instrument and sample availability, no significant isotope fractionation of methane should occur during storage as methane was not consumed or produced between days 14 and 83.
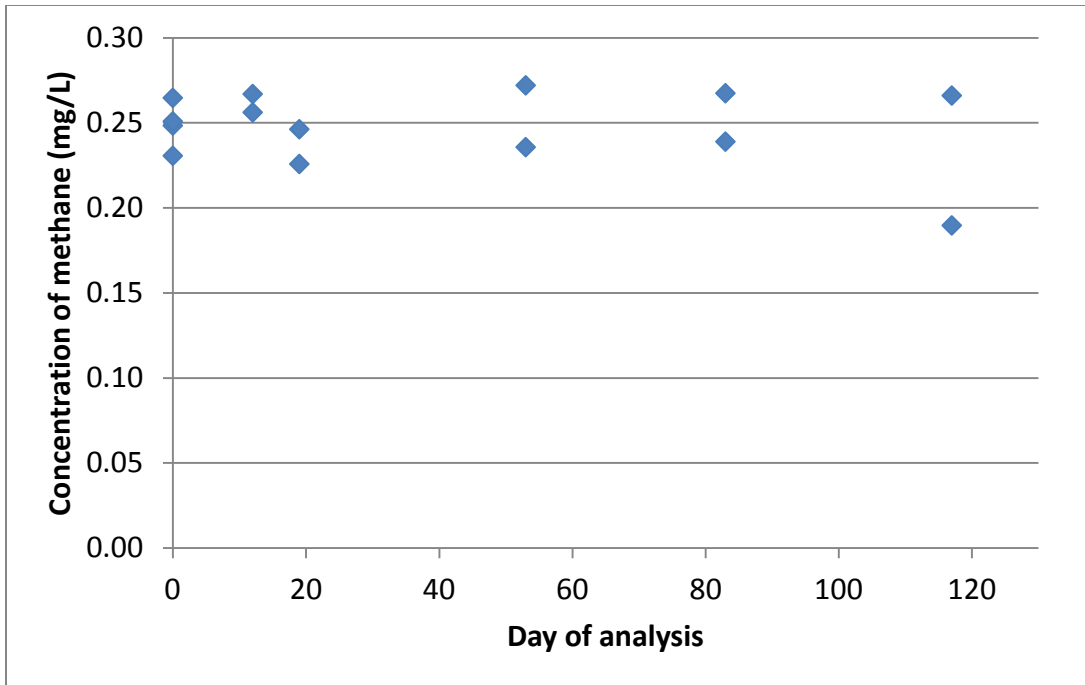
Figure B.1: Effect of preservation time on the precision and accuracy of CH_4 concentration measurements

Appendix C: Stable isotopes and isotopic signature calibration of hydrocarbon gases

As no δ¹³C-certified hydrocarbon gases were available at the start of this project, four hydrocarbon cylinders (one each of 99.0% CH_4, 99.0% C_2H_6 and 99.5% C_3H_8, as well as a 90:5:5% CH_4:C_2H_6:C_3H_8 gas mixture) were purchased from Praxair. Their δ¹³C isotopic signatures were precisely measured in the laboratory using two certified international standards, NBS19 and LSVEC (δ¹³C signatures of 1.95‰ and -46.6‰,[88] respectively). Equation C.1 was used to calibrate the δ¹³C signatures of the hydrocarbon gases from the purchased cylinders:

$$\delta^{13}C_{sample} = \left(\left(\left(\frac{^{13}C}{^{12}C} \right)_{sample} \middle/ \left(\frac{^{13}C}{^{12}C} \right)_{standard} \right) - 1 \right) \times 1000 \qquad (C.1)$$

The δ¹³C notation compares the ¹³C/¹²C ratio of a sample to that of a standard and is reported in ‰. In this equation, the sample refers to the CO_2 produced from the oxidation of methane, ethane and propane, and the standard refers to the CO_2 produced from LSVEC and NBS19. Once calibrated, the hydrocarbon gases were used as an isotopic reference (Table C.1) for the analysis of the samples.

Table C.1: Calibrated $\delta^{13}C$ signatures of the gases used as isotopic references in this

work

$\delta^{13}C$	CH_4	C_2H_6	C_3H_8	MIX
n	6	8	5	6
Average (‰)	-40.90	-29.79	-34.33	-39.30
Stdev (‰)	0.17	0.19	0.23	0.62

Appendix D: Calculations of hydrocarbon gas concentrations in water

The hydrocarbon gas concentrations in the samples were calculated based on equations from Kampbell & Vandergrift (1998).[87] Briefly, the concentration of gas is first calculated in the headspace created in the bottle, at equilibrium. Then, the headspace concentration is used to calculate a dissolved gas concentration in the liquid phase. The two calculated concentrations are then added to provide the total hydrocarbon concentration in the original sample.

First, the partial pressure (p_g) was calculated using the area of the gas measured and the 5-level calibration curves (Equation D.2).

$$p_g = \frac{Area}{Slope} \qquad\qquad (D.2)$$

The concentration of gas in the headspace was then calculated using Equation D.3.

$$C_h = \frac{p_g}{H} \times 55.5 \times MW \times 1000 \qquad\qquad (D.3)$$

Where: C_h is the concentration of gas in the headspace in mg of gas per liter of water

H is the Henry's constant for the gas analyzed in atm per mol fraction

55.5 is the number of moles of water in one liter of water

MW is the molecular weight of the gas analyzed in g per mol

1000 is the conversion from g to mg

The concentration of gas dissolved in the liquid phase was calculated using Equation D.4.

$$C_l = \left(\frac{V_h}{V_t - V_h}\right) \times p_g \times \frac{MW}{22.4} \times \frac{273.15}{T_S} \times 1000 \qquad (D.4)$$

Where: C_l is the concentration of gas in the liquid phase in mg of gas per L of water

V_h is the volume of headspace in mL

V_t is the total volume of the sample in mL

22.4 is the number of liter occupied by an ideal gas at 1 atm and 273.15 K

273.15 is the standard temperature in K

T_S is the sample temperature in K

1000 in the conversion factor from g to mg

Finally the total concentration of gas in the sample was calculated using Equation D.5.

$$C_t = C_h + C_l \qquad (D.5)$$

Where: C_t is the total concentration of gas in the sample in mg of gas per L of water.

Appendix E: Raw data

Table E.1: Raw values of δ¹³C of methane and methane, ethane, propane concentrations

Sample	Date sampled	Latitude (N) (deg)	Longitude (W) (deg)	Methane δ¹³C (‰)	[Methane] (mg/L)		[Ethane] (mg/L)		[Propane] (mg/L)	
					Average	St. Dev.	Average	St. Dev.	Average	St. Dev.
ROC09	Nov. 2012	46.3260	-72.4686	-63.7	45.9131	0.8070	0.0302	0.0007	*0.0010*	0.0004
INRS183	Oct. 2012	45.6795	-73.3784	-62.3	36.7042	1.7589	0.0130	0.0005	*<0.0010*	
INRS224	Sept. 2012	45.4703	-73.2405	-58.5	34.3657	4.1561	0.0229	0.0024	*<0.0010*	
BEC101	May 2013	46.2760	-72.1687	-55.9	32.7058	2.2563	0.0201	0.0004	*<0.0010*	
INRS P14	Oct. 2012	45.8806	-72.7642	-70.7	27.8271	3.3742	0.0080	0.0006	*<0.0010*	
INRS256	Oct. 2012	45.2003	-73.2218	-36.4	26.4235	0.7747	0.0468	0.0014	*<0.0010*	
INRS177	Oct. 2012	45.5016	-73.2942	-57.1	25.6558	2.8330	0.0088	0.0002	*<0.0010*	
INRS256	May 2013	45.2003	-73.2218	-43.1	25.1942	1.8520	0.0224	0.0016	*<0.0010*	
INRS P13	Oct. 2012	45.6385	-73.3146	-56.2	23.0308	1.9537	0.0070	0.0004	*<0.0010*	
BEC121	May 2013	46.1638	-72.3861	-64.5	22.7753	1.5596	0.0258	0.0017	*<0.0010*	
BEC119	Aug. 2012	46.5095	-72.0529	-82.2	19.7226	3.1418	0.0034	0.0005	*<0.0010*	
BEC101	Aug. 2012	46.2760	-72.1687	-55.0	19.0988	3.9217	0.0178	0.0038	*<0.0010*	
NSF018	Nov. 2012	45.9658	-72.6805	-77.3	18.9949	0.2204	0.0047	0.0002	*0.0028*	0.0017
BEC121	Aug. 2012	46.1638	-72.3861	-63.7	17.7697	2.2668	0.0261	0.0011	*<0.0010*	
BEC007	Aug. 2012	46.4002	-72.0811	-70.0	17.0403	0.5398	0.0112	0.0004	*<0.0010*	
NSF015	Nov. 2012	45.9298	-72.4241	-45.6	14.2600	0.1071	0.0089	0.0001	*<0.0010*	
INRS P23	Oct. 2012	45.3686	-73.3330	-56.1	11.6055	0.4158	0.0864	0.0029	0.0030	0.0001
BEC014	Aug. 2012	46.4462	-71.9849	-61.2	9.3716	0.4462	0.0096	0.0005	*<0.0010*	

INRS276	Oct. 2012	45.8032	-72.8085	-55.6	8.9566	0.1972	0.0045	0.0001	*<0.0010*	
NSF003	May 2013	45.9734	-72.5478	-49.9	8.9497	0.0797	0.0047	0.0001	*<0.0010*	
NSF003	Oct. 2012	45.9734	-72.5478	-35.9	8.8224	0.2303	0.0063	0.0002	*<0.0010*	
INRS214	Oct. 2012	45.7183	-72.7501	-60.0	7.6406	0.5960	0.0017	0.0001	*<0.0010*	
INRS155	Oct. 2012	45.0332	-72.4396	-67.6	5.3304	0.0437	0.0702	0.0006	*<0.0010*	
INRS278	Oct. 2012	45.2847	-73.2228	-55.2	5.2205	0.1203	0.0049	0.0002	*<0.0010*	
INRS129	Oct. 2012	45.5638	-72.9821	-103.8	5.1290	0.4491	*0.0006*	<0.0001	*<0.0010*	
INRS280	Oct. 2012	45.2131	-73.0843	-43.2	4.6932	0.3135	0.0022	0.0001	*<0.0010*	
INRS280	May 2013	45.2131	-73.0843	-40.6	4.6773	0.1504	0.0021	0.0001	*<0.0010*	
NSF014	Nov. 2012	46.0977	-72.5434	-72.3	3.3103	0.0771	0.0036	0.0001	*<0.0010*	
BEC204	May 2013	46.5503	-71.9806	-82.4	2.6849	0.0706	0.0012	<0.0001	*<0.0010*	
INRS221	Oct. 2012	45.3914	-73.2648	-64.6	2.5151	0.0711	*<0.0004*		*<0.0010*	
INRS285	Oct. 2012	45.7924	-72.6763	-60.0	2.4840	0.0645	*0.0004*	<0.0001	*<0.0010*	
BEC126	Aug. 2012	46.3040	-71.5454	-59.4	2.4839	0.1013	0.0011	<0.0001	*<0.0010*	
BEC016	Sept. 2012	46.4876	-71.9311	-71.4	2.3812	0.0488	0.0021	0.0001	*<0.0010*	
BEC122	Aug. 2012	46.1177	-72.3803	-64.3	2.0081	0.3554	*0.0009*	0.0002	*<0.0010*	
NSF024	May 2013	46.0111	-72.6778	-73.2	1.5409	0.1170	*0.0004*	0.0001	*<0.0010*	
BEC009	Aug. 2012	46.2512	-72.0076	-103.6	1.3400	0.0905	*0.0005*	<0.0001	*<0.0010*	
NSF012	Nov. 2012	46.0031	-72.0896	-105.1	1.1734	0.0919	*0.0004*	0.0001	0.0043	0.0019
INRS131	Oct. 2012	45.6926	-72.9184	-90.5	1.1531	0.0360	*0.0006*	<0.0001	*<0.0010*	
BEC102	Aug. 2012	46.4898	-72.0291	-89.3	0.9621	0.0579	*0.0005*	0.0001	*<0.0010*	
BEC056	Sept. 2012	46.2507	-72.2490	-60.4	0.8053	0.0230	0.0012	0.0002	*<0.0010*	
BEC120	Aug. 2012	46.1913	-72.4866	-41.2	0.7301	0.0110	*<0.0004*		*<0.0010*	
NSF007	Oct. 2012	46.0637	-72.4853	-79.0	0.7230	0.0531	*<0.0004*		*0.0012*	0.0002
BEC110	Aug. 2012	46.1853	-72.5012	-85.7	0.6725	0.0808	*<0.0004*		*<0.0010*	
NSF004	Oct. 2012	45.8652	-72.4245	-88.7	0.6387	0.0376	*0.0004*	0.0001	0.0036	0.0025
BEC201	Sept. 2012	46.5731	-71.8048	-64.0	0.6015	0.0199	*<0.0004*		*<0.0010*	
BEC103	Aug. 2012	46.1482	-72.3201	-55.9	0.4203	0.0864	*<0.0004*		*<0.0010*	

BEC036	Aug. 2012	46.2096	-71.7896	-33.8	0.3648	0.0035	0.0036	<0.0001	<0.0010	
ROC04	Oct. 2012	46.3822	-71.8462	-76.5	0.3407	0.0114	0.0010	0.0001	*0.0013*	
NSF006	Oct. 2012	45.8199	-72.4756	-79.6	0.3255	0.0096	*0.0004*	0.0001	0.0061	0.0039
BEC002	Aug. 2012	46.3006	-72.0791	-58.0	0.2657	0.0264	*<0.0004*		*<0.0010*	
ROC05	Nov. 2012	46.4507	-71.9141	-77.2	0.2541	0.0143	*0.0004*	0.0001	*<0.0010*	
BEC005	Aug. 2012	46.1819	-72.0787	-24.8	0.2160	0.0110	*0.0005*	0.0005	*<0.0010*	
BEC015	Sept. 2012	46.5282	-71.9249	-75.9	0.1868	0.0168	*<0.0004*		*<0.0010*	
INRS234	May 2013	45.3474	-73.1205	-59.2	0.1780	0.0038	*<0.0004*		*<0.0010*	
BEC021	Aug. 2012	46.3237	-71.9511	-48.0	0.1714	0.0176	*<0.0004*		*<0.0010*	
NSF016	Nov. 2012	45.7585	-72.4951	-75.0	0.1658	0.0080	*<0.0004*		*<0.0010*	
BEC145	Aug. 2012	46.1739	-72.4253	-35.0	0.1325	0.0057	*<0.0004*		*<0.0010*	
INRS234	Oct. 2012	45.3474	-73.1205	-53.1	0.1192	0.0047	*<0.0004*		*<0.0010*	
BEC105	Aug. 2012	46.3643	-72.0012	-53.3	0.1177	0.0164	*<0.0004*		*<0.0010*	
ROC07	Oct. 2012	46.5162	-71.9733	-71.6	0.1040	0.0051	*0.0004*	0.0001	*<0.0010*	
NSF019	Nov. 2012	45.8652	-72.2522	-86.3	0.1017	0.0422	*<0.0004*		*<0.0010*	
INRS233	Oct. 2012	45.3671	-72.9934	-53.7	0.0988	0.0018	*<0.0004*		*<0.0010*	
INRS188	Oct. 2012	45.7149	-73.2446	-56.0	0.0937	0.0028	*<0.0004*		*<0.0010*	
BEC111	Aug. 2012	46.2380	-72.2171	-46.3	0.0890	0.0148	*<0.0004*		*<0.0010*	
NSF017	May 2013	45.8182	-72.5180	-55.3	0.0861	0.0039	*<0.0004*		*<0.0010*	
BEC148	Aug. 2012	46.3266	-71.7726	-73.0	0.0834	0.0106	*<0.0004*		*<0.0010*	
BEC108	Aug. 2012	46.2232	-72.4103	-62.9	0.0830	0.0147	*<0.0004*		*<0.0010*	
INRS210	Oct. 2012	45.5464	-72.8295	-39.9	0.0784	0.0021	*<0.0004*		*<0.0010*	
INRS240	Oct. 2012	45.1667	-72.9651	-43.2	0.0780	0.0039	*<0.0004*		*<0.0010*	
RS01	Nov. 2012	45.9511	-73.0930	*N.D.*	0.0756	0.0032	*<0.0004*		*<0.0010*	
BEC105	May 2013	46.3643	-72.0012	-61.3	0.0751	0.0048	*<0.0004*		*<0.0010*	
INRS P06	Oct. 2012	45.6754	-72.5849	-71.8	0.0628	0.0194	*<0.0004*		*<0.0010*	
INRS227	Oct. 2012	45.4740	-73.0205	-43.4	0.0604	0.0066	*<0.0004*		*<0.0010*	
TR005	May 2013	46.3068	-72.6489	-75.1	0.0595	0.0048	*<0.0004*		*<0.0010*	

BEC031	Aug. 2012	46.2052	-71.9200	-50.9	0.0460	0.0032	*<0.0004*		*<0.0010*	
BEC109	Aug. 2012	46.3447	-72.1510	-49.2	0.0454	0.0098	*<0.0004*		*<0.0010*	
BEC144	Aug. 2012	46.1985	-72.4551	*N.D.*	0.0431	0.0018	*<0.0004*		*<0.0010*	
BEC028	Aug. 2012	46.1134	-72.0590	-49.2	0.0397	0.0012	*<0.0004*		*<0.0010*	
NSF002	Oct. 2012	46.1144	-71.9241	-49.8	0.0392	0.0012	*<0.0004*		*<0.0010*	
BEC036	May 2013	46.2096	-71.7896	-33.4	0.0376	0.0016	*0.0008*	0.0001	*<0.0010*	
NSF008	Oct. 2012	45.9867	-72.2550	-49.2	0.0323	0.0030	*<0.0004*		*<0.0010*	
INRS232	Oct. 2012	45.2879	-73.0143	-34.7	0.0320	0.0006	*<0.0004*		*<0.0010*	
BEC034	Aug. 2012	46.2415	-71.8509	-47.0	0.0291	0.0018	*<0.0004*		*<0.0010*	
INRS212	Oct. 2012	45.5783	-72.7415	*N.D.*	0.0257	0.0022	*<0.0004*		*<0.0010*	
INRS199	Oct. 2012	45.4843	-72.7165	*N.D.*	0.0240	0.0007	*<0.0004*		*<0.0010*	
NSF021	May 2013	45.9552	-72.0059	*N.D.*	0.0214	0.0002	*<0.0004*		*<0.0010*	
NSF005	Oct. 2012	45.8513	-72.3870	*N.D.*	0.0205	0.0008	*<0.0004*		*<0.0010*	
INRS P03	Oct. 2012	45.8723	-72.9128	*N.D.*	0.0176	0.0002	*<0.0004*		*<0.0010*	
BEC147	Aug. 2012	46.3475	-71.8162	*N.D.*	0.0174	0.0015	*<0.0004*		*<0.0010*	
BEC107	Aug. 2012	46.2156	-72.2478	*N.D.*	0.0167	0.0019	*<0.0004*		*<0.0010*	
NSF009	Oct. 2012	45.9215	-72.1845	*N.D.*	0.0163	0.0009	*<0.0004*		*0.0010*	0.0004
INRS251	Oct. 2012	45.1505	-73.3982	*N.D.*	0.0140	0.0004	*<0.0004*		*<0.0010*	
BEC124	Aug. 2012	46.2505	-71.6002	*N.D.*	0.0133	0.0019	*<0.0004*		*<0.0010*	
INRS109	Oct. 2012	45.3422	-72.7704	*N.D.*	0.0120	0.0007	*<0.0004*		*<0.0010*	
INRS149	Oct. 2012	45.5753	-72.5950	*N.D.*	0.0116	0.0009	*<0.0004*		*<0.0010*	
INRS115	Oct. 2012	45.2247	-72.7711	*N.D.*	0.0115	0.0012	*<0.0004*		*<0.0010*	
INRS300	Oct. 2012	45.2726	-72.9264	*N.D.*	0.0112	0.0009	*<0.0004*		*<0.0010*	
INRS164	Oct. 2012	45.5391	-72.3619	*N.D.*	0.0106	0.0014	*<0.0004*		*<0.0010*	
BEC100	Aug. 2012	46.2605	-72.0734	*N.D.*	0.0103	0.0005	*<0.0004*		*<0.0010*	
INRS P08	Oct. 2012	45.8783	-73.1290	*N.D.*	0.0099	<0.0001	*<0.0004*		*<0.0010*	
BEC030	Aug. 2012	46.1633	-71.9367	*N.D.*	0.0093	0.0010	*<0.0004*		*<0.0010*	
INRS270	Oct. 2012	45.4485	-72.8907	*N.D.*	0.0089	0.0012	*<0.0004*		*<0.0010*	

Site	Date	Latitude	Longitude							
INRS213	Oct. 2012	45.5502	-72.6689	*N.D.*	0.0082	0.0004	*<0.0004*		*<0.0010*	
BEC130	Aug. 2012	46.1754	-71.7683	*N.D.*	0.0076	0.0004	*<0.0004*		*<0.0010*	
ROC02	Oct. 2012	46.2970	-71.7540	*N.D.*	0.0076	0.0008	*<0.0004*		*<0.0010*	
TR002	April 2013	46.4244	-72.6024	*N.D.*	0.0071	0.0004	*<0.0004*		*<0.0010*	
BEC140	Aug. 2012	46.0830	-71.6063	*N.D.*	0.0070	0.0010	*<0.0004*		*<0.0010*	
INRS P10	Oct. 2012	45.0656	-72.8721	*N.D.*	0.0068	0.0002	*0.0004*	0.0001	*<0.0010*	
INRS MSH	Oct. 2012	45.5396	-73.1545	*N.D.*	0.0047	<0.0001	*<0.0004*		*<0.0010*	
NSF020	May 2013	45.9833	-72.3439	*N.D.*	0.0045	<0.0001	*<0.0004*		*<0.0010*	
INRS143	Oct. 2012	45.3330	-72.5044	*N.D.*	0.0042	0.0003	*<0.0004*		*<0.0010*	
NSF011	Nov. 2012	45.9798	-71.8084	*N.D.*	0.0039	0.0003	*<0.0004*		*<0.0010*	
BEC117	Aug. 2012	46.5447	-72.1083	*N.D.*	0.0037	0.0005	*<0.0004*		*<0.0010*	
BEC010	Sept. 2012	46.2696	-71.9328	*N.D.*	0.0036	0.0003	*<0.0004*		*<0.0010*	
TR001	April 2013	46.3712	-72.6709	*N.D.*	0.0032	0.0001	*<0.0004*		*<0.0010*	
NSF013	Nov. 2012	46.0257	-72.7098	*N.D.*	0.0030	0.0022	*<0.0004*		*<0.0010*	
CHM001	May 2013	46.4398	-72.4023	*N.D.*	0.0024	0.0003	*<0.0004*		*<0.0010*	
BEC029	Aug. 2012	46.1703	-71.9967	*N.D.*	0.0023	<0.0001	*<0.0004*		*<0.0010*	
SLV001	May 2013	46.4926	-72.4264	*N.D.*	0.0021	<0.0001	*<0.0004*		*<0.0010*	
INRS169	Oct. 2012	45.4292	-72.3846	*N.D.*	0.0020	0.0001	*<0.0004*		*<0.0010*	
BEC132	Aug. 2012	46.1497	-71.6994	*N.D.*	*0.0009*	0.0003	*<0.0004*		*<0.0010*	
BEC139	Aug. 2012	46.3384	-71.5552	*N.D.*	*0.0008*	0.0001	*<0.0004*		*<0.0010*	
TR004	April 2013	46.3764	-72.5334	*N.D.*	*0.0007*	<0.0001	*<0.0004*		*<0.0010*	
NSF023	May 2013	45.6700	-72.3384	*N.D.*	*0.0007*	0.0002	*<0.0004*		*<0.0010*	
TR003	April 2013	46.4053	-72.6113	*N.D.*	*0.0007*	0.0003	*<0.0004*		*<0.0010*	
BEC032	Oct. 2012	46.1667	-71.8577	*N.D.*	*<0.0006*		*<0.0004*		*0.0011*	0.0003
BEC104	Nov. 2012	46.1053	-72.2579	*N.D.*	*<0.0006*		*<0.0004*		*<0.0010*	
BEC106	Aug. 2012	46.3680	-72.2271	*N.D.*	*<0.0006*		*<0.0004*		*<0.0010*	
BEC114	Aug. 2012	46.2963	-71.6631	*N.D.*	*<0.0006*		*<0.0004*		*<0.0010*	
BEC127	Aug. 2012	46.2743	-71.4896	*N.D.*	*<0.0006*		*<0.0004*		*<0.0010*	

BEC149	Aug. 2012	46.2562	-71.8032	*N.D.*	*<0.0006*	*<0.0004*	*<0.0010*
BEC203	Sept. 2012	46.4132	-72.1138	*N.D.*	*<0.0006*	*<0.0004*	*<0.0010*
INRS263	Oct. 2012	45.0174	-72.6596	*N.D.*	*<0.0006*	*<0.0004*	*<0.0010*
INRS269	Oct. 2012	45.1346	-72.5100	*N.D.*	*<0.0006*	*<0.0004*	*<0.0010*
NSF001	Oct. 2012	46.0344	-71.9251	*N.D.*	*<0.0006*	*<0.0004*	*<0.0010*
NSF010	Nov. 2012	46.1009	-71.8073	*N.D.*	*<0.0006*	*<0.0004*	*<0.0010*
NSF022	May 2013	45.8411	-72.0911	*N.D.*	*<0.0006*	*<0.0004*	*<0.0010*
ROC01	Oct. 2012	46.2019	-71.6186	*N.D.*	*<0.0006*	*<0.0004*	*<0.0010*

* N.D.: Not determined because concentrations were below the limit of detection.