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# A systematic multi-isotope approach to unravel methane origin in groundwater: example of an aquifer above a gas field in southern New Brunswick (Canada)

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## Abstract

Following the large increase in unconventional hydrocarbon production in North America and elsewhere in the last 15 years, many jurisdictions have implemented groundwater monitoring programs to verify whether these subsurface industrial activities impact shallow groundwater quality. The interpretation of groundwater monitoring results typically relies mostly on dissolved alkane chemical and isotopic composition to infer the potential presence of thermogenic hydrocarbons presumed to originate from a deep source, which may indicate contamination. However, ambiguous results are frequently obtained, and post-genetic processes are often suspected to have modified the original gas composition. Here, we present a systematic approach to identify alkane origin with greater certainty, by thoroughly investigating four processes that may affect dissolved hydrocarbon gas: 1) late-stage methanogenesis, 2) oxidation (of methane or higher alkanes), 3) mixing between different gas sources, and 4) secondary methanogenesis. This is achieved by using empirical equations and fractionation factors available in the literature, combined to site-specific isotopic tracers ($\delta^{13}C_{CH4}$, $\delta^{2}H_{CH4}$, $\delta^{2}H_{H2O}$, $\delta^{13}C_{DIC}$) in groundwater samples. This approach is being tested and applied to a study area located in southern New Brunswick, Canada. The area overlies the McCully gas field from which unconventional natural gas is produced since 2003, and the nearby Elgin area, a prospective area for condensates. Results demonstrate that the presence of methane in groundwater is not related to the proximity of gas wells. In a few shallow wells located very close to producing gas wells in the McCully gas field, methane and ethane were detected, and the compositional and isotopic data sometimes seemed to point towards a thermogenic origin. However, consideration of the four processes led to the conclusion that the gas was of microbial origin, and that it had been oxidized to various levels. In contrast, thermogenic gas was detected in groundwater in the Elgin area, where no commercial production has yet taken place. In this area the natural hydrocarbon gas context is more complex, and the gas from some of the wells was affected by mixing, oxidation, and late-stage methanogenesis. Finally, the approach used in this paper has proven capable of disentangling the original isotopic signature from post-genetic modifications and, despite initial ambiguity, has shown no evidence that past hydraulic fracturing in the McCully gas field has affected shallow groundwater quality.

**Keywords: dissolved hydrocarbons; isotopes; Frederick Brook; Hiram Brook; unconventional hydrocarbon production**

## 1 Introduction

Unconventional production of oil and natural gas (O&G) involving hydraulic fracturing has undergone a tremendous increase in North America since the beginning of the 2000’s (Jarvie, 2012a, b). Most shale gas plays contain hydrocarbons of thermogenic origin, meaning that they were created by the thermal conversion of organic matter under deep burial conditions of high temperatures and pressures (Barker, 1990; Hunt, 1979). Alternatively, natural gas can be produced at lower temperatures and pressures by methanogenic microorganisms which can convert either $CO_2$ or methylated substrates (most often acetate) to methane (Deppenmeier, 2002) under anoxic conditions at redox levels of Eh lower than -200 mV (Conrad, 2020; Whiticar, 1999). Such microbial gas is typically produced closer to the ground surface, and is ubiquitous and indigenous in many shallow aquifers (Whiticar et al., 1986). Lastly, methane can have an abiotic origin, being formed entirely by chemical reactions that do not directly involve organic matter (Etiope and Sherwood-Lollar, 2013). Abiotic methane occurs in particular environments (e.g. Precambrian crystalline shields, igneous batoliths, geothermal fluids, hyperalkaline springs; Milkov and Etiope, 2018), which are not representative of the study area presented here.

In unconventional O&G plays, hydrocarbons are entrapped within the tight pores of a shale or siltstone/sandstone unit. The wells must be hydraulically fractured (or “fracked”) by injecting a mixture of water, proppants (e.g. sand) and chemicals at high pressures to increase permeability and ease the flow of the hydrocarbons into the wellbore (Lefebvre, 2017). While unconventional O&G production has been deployed rapidly in several regions, there have been public concerns regarding possible environmental impacts, especially in areas without a long history of conventional hydrocarbon exploitation. One of the main environmental and health concerns is whether hydraulic fracturing could cause contamination of shallow groundwater, through upward migration of substances, which are either being injected (fracking fluid) or are naturally present at depth (e.g. natural gas, brines). Theoretically, the “intermediate zone”, which is the thick succession of bedrock units between the O&G reservoir and shallow aquifers, should prevent such migration. However, migration may be possible through either faulty wellbores, abandoned (legacy) O&G wells, or less likely, through structural discontinuities (faults, fractures) that are permeable and span the whole stratigraphic succession between the hydrocarbon reservoir and shallow groundwater (Dusseault and Jackson, 2014; Gassiat et al., 2013). As these risk factors vary geographically and geologically, site-specific studies are needed to determine whether unconventional O&G activities at depth could negatively affect shallow groundwater in a given region. In many jurisdictions, bans (permanent) or moratoria (temporary) on hydraulic fracturing have been put in place, in order to apply the precautionary principle. Moratoria are intended to be in place until sound geoscientific data are available to properly assess health and environmental risks of these technologies (Government of New Brunswick, 2016; Rivard et al., 2014).

This is notably the case in New Brunswick, a Canadian province where several areas have been identified as potential targets for unconventional O&G production (Loomer et al., 2016). O&G exploration was conducted in a few areas, and significant production started in 2003 in the McCully gas field near the town of Sussex, in the southern part of the province. However, public concerns led to a province-wide moratorium on hydraulic fracturing in 2014. Recently, the provincial government considered lifting this moratorium to allow production exclusively in the Sussex area, but uncertainties on the appropriate approaches to fulfill the province’s duty to consult Indigenous people has so far retarded any approval of fracturing (Magee, 2019).

In order to fill the knowledge gaps about the potential incidence of hydraulic fracturing in New Brunswick, three environmental studies have been undertaken between 2011 and 2019 (see Section 2 for details). The first two studies (Al et al., 2013; Brake et al., 2013; Loomer et al., 2018; Loomer et al., 2016) aimed at establishing natural (baseline) groundwater conditions, and thus specifically targeted private water wells that are located away (>1.6 km) from any existing O&G well. These two studies have reported the presence of naturally-occurring methane in several shallow water wells in the study area of the present paper. The third study was carried out by the Geological Survey of Canada (GSC), specifically in the McCully/Elgin area; the present paper reports on the geochemical component of this multidisciplinary project, which globally aimed at assessing aquifer vulnerability in the context of hydraulic fracturing, by evaluating the possibility of upward contaminant migration through preferential pathways. For the first time in this region, the objective of the hydrogeochemical sampling was to determine whether groundwater very close to unconventional gas wells had been impacted by hydraulic fracturing and hydrocarbon production. This paper therefore presents insights from the two objectives of the hydrogeochemical sampling scheme, namely: 1) assessing the presence of hydrocarbons in shallow groundwater, including areas very close to producing gas wells (directly on the well pad, i.e. <75 m from the wellhead); and 2) using a multi-isotope approach to decipher the origin (microbial or thermogenic) of dissolved alkanes in groundwater. By using site-specific data along with equations from the literature, this approach involved investigating four processes that may affect the hydrocarbon gas and mask its true origin, namely: 1) late-stage methanogenesis; 2) oxidation; 3) mixing between thermogenic and microbial gas; and 4) secondary methanogenesis.

The implications of the conclusions from environmental studies conducted to determine the origin of hydrocarbons in groundwater are serious and thus necessitate the adoption of a rigorous and structured approach. Hydrocarbon gases can either be indigenous to an aquifer or to relatively shallow underlying stratigraphic layer, or they could alternatively represent deep-seated gas that has migrated upward either naturally or as a result of hydrocarbon production activities (i.e. stray gas), causing contamination of shallow groundwater resources. Typically, microbial gas can be inferred to be indigenous to an aquifer (or to relatively shallow underlying stratigraphic units), whereas thermogenic gas originates from greater depths, possibly from the unit targeted by the industry. Some exceptions occur, such as deep shale gas-bearing geological formations containing microbial gas (Martini et al., 1998), or inversely, thermogenic gas being present in shallow bedrock that was once buried at great depth (Bordeleau et al., 2018a; Lavoie et al., 2016). Identifying the gas origin has typically been achieved so far by examining: 1) the gas compositional ratio, or “dryness ratio” (dryness ratio= [methane]/[ethane+propane]), knowing that ratios >1000 are typical of microbial gas, and ratios < 100 are typical of thermogenic gas (Bernard, 1978; Milkov and Etiope, 2018); and 2) the isotopic composition of methane ($\delta^{13}C_{CH4}$, $\delta^{2}H_{CH4}$), and comparing with typical isotopic fields described in the literature for microbial and thermogenic gases (Milkov and Etiope, 2018; Whiticar, 1999). This approach theoretically works well for gases that have not been affected (during production) or modified (post-genetically) by biogeochemical processes. Yet, if one or several processes modify the compositional and isotopic signature of the hydrocarbon gas, then microbial gas could resemble thermogenic gas, or vice versa, leading to erroneous conclusions on gas origin. Thoroughly investigating these processes therefore increases the possibility of conclusively identifying the true origin of the hydrocarbon gas.

## 2 Previous baseline studies in this region

The first two environmental studies related to hydrocarbons in New Brunswick covered a vast portion of the province, including the Sussex area. The first one (2011-2015) was carried out by the Geological Survey of Canada, and mostly aimed at defining the unconventional O&G plays and providing a georeferenced database of all publicly-available geological, hydrogeological and exploration data on shale gas units in eastern Canada (Brake et al., 2013). This study included groundwater geochemical data from wells near the McCully gas field and around the town of Elgin (a prospective area for condensates, east of Sussex) to establish local groundwater baseline conditions (Al et al., 2013). The groundwater aspect of the project included the sampling of 24 residential wells, along with 11 brine and six gas samples from producing tight sandstone gas wells located in the McCully gas field. Methane was detected in only three of the shallow wells, at concentrations of 0.01 mg/L (McCully area), 0.11 and 1.17 mg/L (Elgin area); no ethane or propane was detected. There was no apparent correlation between these methane detections and proximity to unconventional O&G wells. Two of the samples had sufficient concentrations to allow $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$ analyses. One of them had an isotopic composition typical of thermogenic gas ($\delta^{13}C_{CH4}$= -49.96‰, $\delta^{2}H_{CH4}$= -158‰), while the other fell outside of usual domains for thermogenic or microbial gas ($\delta^{13}C_{CH4}$= -45.84‰, $\delta^{2}H_{CH4}$= -88‰) and was interpreted as thermogenic gas that had been partially oxidized (Al et al., 2013). As for the deep formation gas, the six samples had dryness ratios between 13 and 52, typical of thermogenic gas. The ion composition of deep brine samples suggest a seawater origin followed by modification through diagenetic processes (dolomitization, ion exchange, sulphate reduction; Al et al., 2013). The ion composition of shallow groundwater was distinct from the brines, and no evidence of deep brine contribution to shallow groundwater was found.

A second study (2014-2016) aimed at establishing baseline conditions in four New Brunswick regions of interest to the petroleum industry, namely the Kent, Central, Shediac, and Sussex areas (Loomer et al., 2018; Loomer et al., 2016). The “Sussex area” surveyed by these authors covered approximately 1,600 km$^2$, and encompassed notably the McCully gas field and the town of Elgin (Fig. 1B). A total of 152 private wells were sampled in this area, and nine of these wells were selected for repeated sampling (monthly samples over one year). Methane was detected in 50% of the sampled wells, usually at concentrations <0.1 mg/L. A few wells (n=19) had higher concentrations, with the highest measured concentration being

28.9 mg/L. Ethane was detected in 13 groundwater samples, and propane was detected in 4 samples. No correlation was found between methane concentrations and topography or proximity to O&G wells. A certain positive correlation was observed between higher methane concentrations and sodic (Na-rich) water. Also, wells with >1 mg/L methane were commonly found where the hydrocarbon-producing Horton Group bedrock was inferred to be at or near the surface (e.g. in the Elgin area). Isotopic analyses were carried out on the 19 samples with sufficient methane concentrations. On a Whiticar (1999) diagram showing $\delta^{13}C_{CH4}$ versus $\delta^{2}H_{CH4}$, most of these wells plot within microbial (sometimes termed "biogenic" in older publications) or mix/transition fields, with a few plotting in the thermogenic field (Loomer et al., 2016). Of note, none of the wells sampled near the McCully gas field had sufficient methane concentration for isotopic analyses.

The third environmental project concerning hydrocarbons in New Brunswick (2015-2019), conducted again by the Geological Survey of Canada, was multidisciplinary and included various components such as shallow (Crow et al., 2017) and deep (Duchesne and Bellefleur, 2019) geophysics, geomechanics (Séjourné, 2017), hydrogeology (Huchet, 2018), tectonostratigraphy (Brake et al., 2019) and rock organic geochemistry (Jiang et al., 2016), in addition to a strong groundwater geochemistry component. The results from the latter are presented in this paper.

## 3 Site description

This project focuses on two small areas located near Sussex in southern New Brunswick (eastern Canada), for a total of 1417 km$^2$ (Fig. 1C). The first of the two areas is the McCully gas field, located 10 km north-east of the town of Sussex (Fig. 1). It is the only active natural gas production area in New Brunswick, and has been exploited by Corridor Resources Inc. (now Headwater Exploration) from 2001 to 2020. Natural gas production from the tight sandstone of the Hiram Brook Member of the Albert Formation (see section 3.1 for the geological context) started in 2003, and hydraulic fracturing was conducted until the moratorium came into place in June 2015. In the McCully gas field, hydraulic fracturing of the tight sandstone differs from the fracturing of typical shale gas wells. Wells are not horizontal but variously inclined and fracturing in the target sandstone unit consists of water- or propane-based fluid under high pressure but low volume of injected fluid with proppants from single or couple of fracking stages (Leblanc et al., 2011). As of 2018, the gas production (57 billion cubic feet to date) relied on 32 wells located on 11 pads (Evaluate Energy, 2018).

The second area is around the town of Elgin, 30 km north-east of Sussex, which is currently a prospective area for condensates. A first petroleum exploratory well was drilled by Corridor Resources Inc. in 1999, with no success (St. Peter, 2000). Starting in 2011, new drilling has shown good potential of the shales of the Frederick Brook Member (also of the Albert Formation). Production would target condensates rather than gas, as the hydrocarbons in this reservoir at shallower depths compared to those in the McCully gas field, are less mature than in the McCully field (Park, 2014).

The whole study area encompasses three counties, with a total population of 247,722 inhabitants (27.7 inhabitants/km$^2$). The land is mainly covered by forest (78%), with some agriculture (20%) and urban areas (2%) (Huchet, 2018). This area covers portions of the watersheds of the Kennebecasis River (McCully area) and the Pollet River (Elgin area). Topography is relatively steep, with several valleys. The Kennebecasis River is south-west oriented, following the main structures of the basin. Climate is humid continental with temperate summers, an average annual temperature of 6.3 $^o$C, and annual precipitation of 1,130 mm/y. Most precipitations occur in May/June, and September/October (Huchet, 2018).

## 3.1 Geology

In Eastern Canada, the late Paleozoic Maritimes Basin lies on the Proterozoic to middle Devonian crystalline basement, which is cut by several major structures. Through various basement upheavals, the Maritimes Basin has been separated into sub-basins, which have then been isolated for most of their geological history (St. Peter and Johnson, 2009). The study area is located in the Moncton sub-basin, where the sedimentary succession consists (from bottom to top) of the Upper Devonian to Lower Carboniferous Horton Group, the Lower Carboniferous Sussex, Windsor and Mabou groups, with the Upper Carboniferous Cumberland and Pictou groups at the top of the sedimentary sequence (Fig. 2).

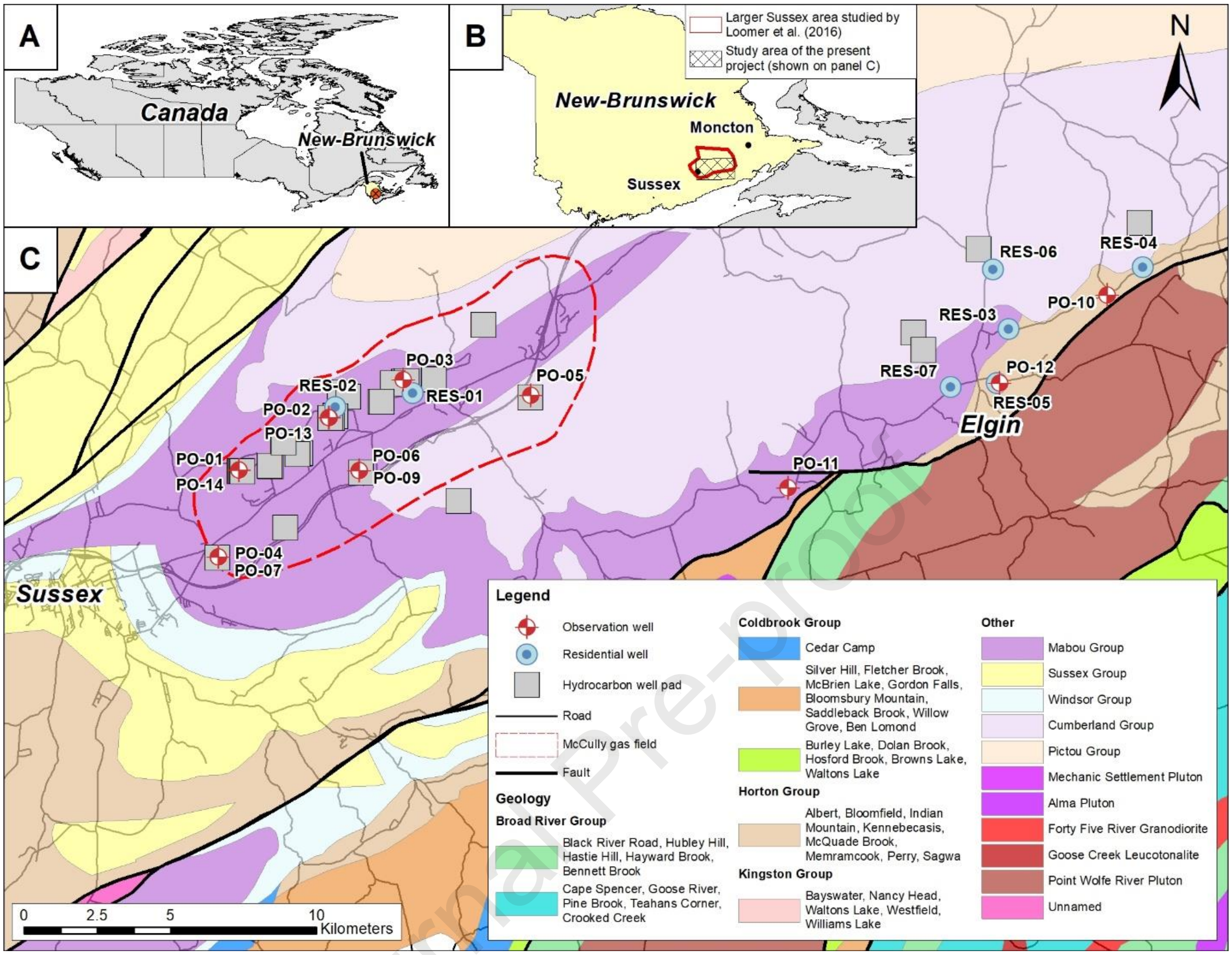

*Figure 1. Location of the study area within Canada (Panel A), and more precisely, within the province of New Brunswick (Panel B). Panel C (close-up view of the study area) shows surficial bedrock geology, position of the sampled wells (residential: RES and observation: PO), and hydrocarbon well pads. Of note, the hydrocarbon wells in the McCully gas field (delimited with red dashed line) have undergone production, while those to the north of the town of Elgin are exploration wells.*

The stratigraphic units of interest to the petroleum industry in the McCully gas field, namely the fine-grained sandstone of the Hiram Brook Member and the shale of the Frederick Brook Member of the Albert Formation, are part of the Horton Group (Fig. 2). In the Elgin area, only the condensates in the shale of the Frederick Brook Member have been targeted. In the McCully gas field, the vertical or inclined wells reach depths of 2 to 4 km. The thickness of the Horton Group varies between 250 and 1,000 m (Hinds and St. Peter, 2006), and the Hiram Brook Member is found between 1,100 and 2,500 m depth, while the Frederick Brook Member occurs between 1,700 and 3,000 m depth (Brake et al., 2019; Séjourné, 2017).

Higher in the stratigraphic succession, the Windsor Group is host to a potash mine, exploited between 1983 and 2015 by Potash Corporation of Saskatchewan Inc.

The sedimentary sequence illustrated on Fig. 2 occurred through six unconformity-bounded depositional cycles between the Upper Devonian and the Upper Carboniferous. Today, all of these units outcrop to various extents throughout the Kennebecassis and Pollet river watersheds (Huchet, 2018). The residential and observation wells sampled in this study are completed in the Cumberland (n=2), Mabou (n=13), Sussex (n=1) and Horton (n=4) groups. The Cumberland Group consists of sandstone and conglomerate; the Mabou Group comprises alternating conglomerate, sandstone and mudstone; the Sussex Group is made up of laterally equivalent coarse conglomerate, sandstone and mudstone and finally the Horton Group consists of alternating black and red mudstone with around 10% fine-grained sandstone and siltstone.

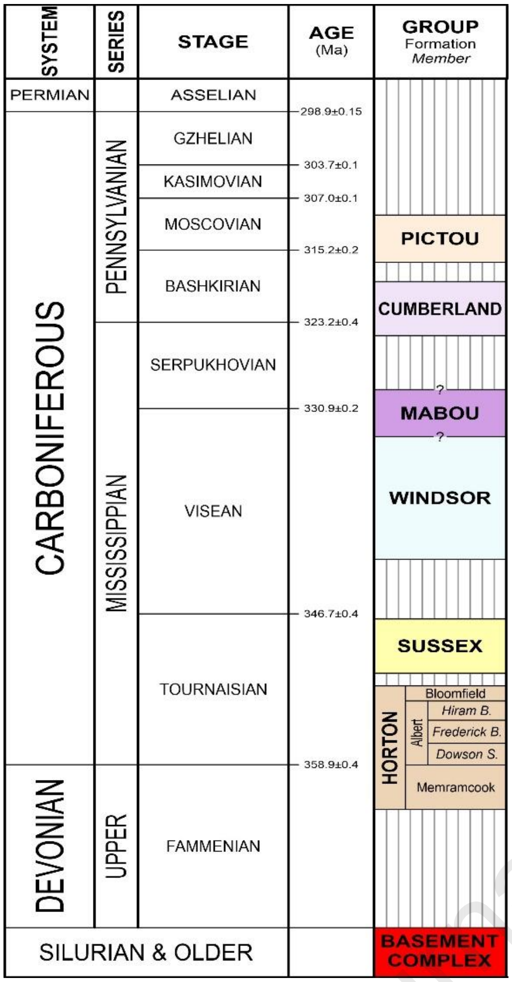

*Figure 2*. Simplified stratigraphy of the study area, modified from St. Peter et al. (2005) and St. Peter and Johnson (2009). Vertical hatched patterns are for non-deposition and unconformity. Bold fonts are for groups and pre-Devonian, normal fonts are for formations and italic fonts are for members. B = Brook; S = Settlement.

### 3.2 Hydrogeology

In the McCully/Elgin study area, the Mabou Group represents the main regional aquifer, and conditions in this highly fractured bedrock aquifer are usually unconfined to semi-confined. Piezometry is controlled by topography, and rivers act as the main discharge zones (Huchet, 2018). Surficial deposits are usually thin and permeable, favouring recharge of the bedrock aquifer. Groundwater recharge is approximately 300 mm/y, and the active flow zone is concentrated in the top 50-100 m below ground surface (Huchet, 2018). The bedrock permeability is mainly fracture-controlled; permeability (slug) tests in eight observation wells provided hydraulic conductivities (K) typically ranging between $10^{-6}$ to $10^{-4}$ m/s, with a median of $1.8 \times 10^{-5}$ m/s.

Drinking water supply in the McCully and Elgin areas occurs mainly through private residential or farm wells, most of which (96.3%) tap the bedrock aquifer (Huchet, 2018). The water table is generally found between 0-20 m below ground surface, and most private wells have depths of 20-60 m. A particular situation occurs on the south bank of the Kennebecasis River in the McCully area, where water levels had reportedly dropped due to pumping in the nearby potash mine. Water supply in this area is now provided by a 107-m deep community well (Huchet, 2018).

## 4 Methodology

### 4.1 General approach

The shallow groundwater characterization for the present study involved sampling a total of 20 water wells, which includes 7 residential water supply wells (named RES-XX), and 13 shallow observation wells drilled for the project (named PO-XX). Residential wells are all located on separate lots throughout the study area. Among the residential wells, one was screened in unconsolidated sediments (RES-05), and the other six were open bedrock wells. All observation wells drilled for the project were also open to bedrock, and the metal casing within the overlying sediment was sealed with bentonite; their depth ranged from 49 to 130 m, the majority being 50 m deep (Appendix A). However, contrary to residential wells, in some cases two observation wells are located on the same site. This occurred in cases where initial intriguing water chemistry and/or observed geology prompted the subsequent drilling of a second well next to the original one, in order to gain additional information. These twin wells (PO-01/PO-14, PO-02/PO-13, PO-04/PO-07, and PO-06/PO-09) have each been sampled throughout the study.

To assess the influence of producing gas well proximity on groundwater quality, the sampled water wells were selected to be either “very close to”, or “far from” any existing O&G well. “Very close” observation wells (n=10) are located directly on producing gas well pads, within 75 m of the wellhead. Some residential wells (n=2) are also relatively close to gas wells (within 400 m). All other sampled water wells are located “far from” (i.e. >1.6 km) any gas well where hydraulic fracturing has occurred.

Water samples collected in each well during their first sampling were analyzed for metals and other cations, anions, dissolved inorganic carbon (DIC), volatile organic compounds (VOCs), $C_1$-$C_3$ alkanes (methane, ethane, propane), and isotopic composition of water ($\delta^2H_{H2O}$, $\delta^{18}O_{H2O}$), DIC ($\delta^{13}C_{DIC}$), and methane ($\delta^{13}C_{CH4}$, $\delta^2H_{CH4}$). These parameters were used for geochemical interpretation, but also to verify compliance with the drinking water guidelines from the New Brunswick Office of the Chief Medical Officer of Health (OCMOH, 2020) and Health Canada (2019). Physico-chemical parameters (temperature, pH, dissolved oxygen (DO), redox potential (ORP), electrical conductivity) were measured on-site. Concentrations of bicarbonate ($HCO_3^-$) and total dissolved solids (TDS), as well as water type, were computed using chemical and physico-chemical data. To define water types, the charge balance was first verified for each sampling point by computing the concentrations (in meq/L) of major cations ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$) and anions ($Cl^-$, $SO_4^{2-}$, and $HCO_3^-$). The tolerance ([cations-anions]/[cations+anions]) to consider an analysis valid was set at ±10%.

To establish the range of values (concentrations and isotopic composition) that can be expected in each of the wells, most of them were sampled several times, at various times of the year, for a total number of samples per well between 3 and 10, over a period of 33 months (December 2015 to August 2018). Subsequent samples collected at given wells were analyzed for a restricted number of compounds, usually alkane and DIC concentrations, and isotopic composition of DIC and methane, as well as physico-chemical parameter measurements. Three of the wells (RES-07, PO-13, PO-14) were included towards the end of the project to obtain more information in a given area, and were sampled only once.

## 4.2 Sampling techniques

Samples from residential wells were collected upstream from any water treatment system. The wells were purged until field physico-chemical parameters were stable over three measurements taken at 5 minute intervals. After purging, the flow rate was lowered to a minimum and a 6.25 mm (¼'') diameter tube was connected to the garden hose spigot to allow sampling while minimizing water turbulence and degassing.

All observation wells except PO-02 (see further) were sampled using a submersible pump (Redi-Flo2 from Grundfos, Denmark) with a 6.25 mm (¼'') tubing for water extraction. The pump was carefully lowered in the well until the desired depth (see Table 1), where the most productive fractures had previously been identified using downhole geophysical surveys (Crow et al., 2017). In order to target water coming from the desired fracture zone and to minimize drawdown, sampling was carried out at a low flow, i.e. below 500 mL/min, as recommended by the United States Environmental Protection Agency (Puls and Barcelona, 1996). Purging was carried out until physico-chemical parameters stabilized. The only observation well that was not sampled with a pump is PO-02, because it was artesian flowing. A water-tight cap equipped with a ball valve was installed on the wellhead; for sampling, the valve was opened, and water was sampled directly from a tube connected to the valve, after stabilization of physico-chemical parameters.

When sampling residential and observation wells, water for most chemical analyses was simply poured into the appropriate bottles, after rinsing three times. For analyses of DIC and metals, samples were filtered using a 0.45 µm nylon membrane. For analysis of alkane concentrations and isotopic composition, the submerged container method was used, as recommended by the United States Geological Survey (USGS, 2017).

Bottles/vials were kept refrigerated at all times. Preservation of samples for metals and alkane analyses was ensured by the presence of acid in the bottles, resulting in a pH <2. All sample preservation times prescribed by the laboratories were respected; samples for alkanes were always analyzed within 10 days of sampling.

## 4.3 Analytical methods

Metals (Al, Sb, Ag, As, Ba, Be, Bi, B, Cd, Ca, Cr, Co, Cu, Sn, Fe, Li, Mg, Mn, Mo, Ni, Pb, K, Se, Si, Sr, Na, U, Ti, V, Z) were analyzed using an Agilent (Santa Clara, CA) 7700X ICP-MS. Major ions ($Br^-$, $Cl^-$, $NO_2^-$+$NO_3^-$, $SO_4^{2-}$) were analyzed using a Dionex (Sunnyvale, CA) ICS-1600 ion chromatograph. Alkalinity was analyzed using a Mantech (Guelph, ON) PC-Titrate auto-analyzer. These analyses were performed in a certified commercial laboratory (Maxxam Analytics, Québec, QC). Concentrations of DIC were determined at the Institut national de la recherche scientifique (Québec, QC) using a Shimadzu total carbon (TOC) analyzer.

Concentrations of dissolved $C_1$-$C_3$ alkanes were determined at the Delta-Lab of the Geological Survey of Canada (Québec, QC) using a Stratum PTC (Teledyne Tekmar, Mason, OH) purge and trap concentrator system interfaced with an Agilent (Santa Clara, CA) 7890 gas chromatograph equipped with a flame ionisation detector (GC-FID). The method employed was adapted from Pennsylvania Department of Environmental Protection method 3686 (PA-DEP, 2012) and US EPA method RSK 175 (Kampbell and Vandegrift, 1998). Detection limits on our samples were 0.006, 0.002, and 0.01 mg/L for methane, ethane and propane, respectively. The precision based on repeated injections is better than 15%.

Water stable isotopic composition ($\delta^2H_{H2O}$, $\delta^{18}O_{H2O}$) was analyzed using Delta plus XP + (Thermo Fisher Scientific, Bremen, Germany) isotope ratio mass spectrometer (IRMS) hyphenated to a Gasbench at the Ján Veizer Stable Isotope Laboratory of the University of Ottawa (ON), and results are presented in the usual delta (δ) notation expressed in per mil (‰) relative to the international Vienna Mean Standard Ocean Water (VSMOW) reference. Precision is ±2‰ for $\delta^2$H and ±0.15‰ for $\delta^{18}$O.

Isotopic analyses of DIC ($\delta^{13}C_{DIC}$) were done at the University of Waterloo (ON), using a Gilson (Middleton, WI) 222XL auto-sampler and a MicroGas (IsoPrime,Manchester, UK) IRMS. The isotopic composition of samples is expressed in the usual per mil notation relative to the international Vienna Pee Dee Belemnite (VPDB) standard. Precision is ± 0.2‰.

Isotope ratios of methane ($\delta^{13}C_{CH4}$, $\delta^2H_{CH4}$) were measured at the Delta-Lab of the Geological Survey of Canada, using a TRACE 1310 GC equipped with an Agilent J&W GS-Carbonplot column (30 m × 0.32 mm × 3.0 µm) interfaced with a Delta V IRMS via a GC IsoLink system (Thermo Fisher Scientific, Bremen, Germany). The detailed protocol is presented in Appendix B. The isotopic compositions of samples are expressed in the usual per mil notation relative to VPDB ($\delta^{13}$C) or VSMOW ($\delta^2$H) standards. The uncertainty due to sampling, handling and analytical procedures is ±1.7‰ for $\delta^{13}$C and ±19‰ for $\delta^2$H (Rivard et al., 2018).

# 5 Results

## 5.1 General groundwater chemistry

None of the analyzed metals, anions or VOCs exceeded the drinking water guidelines from OCMOH (2020) or Health Canada (2019), in any of the sampled wells. TDS was variable (96 to 1994 mg/L), but was unrelated to proximity to O&G wells. General chemistry data was used to define water types, based on dominant cation(s) and anion(s) in samples. Among all sampled wells, 8 water types were identified, namely: Mg-$HCO_3$-Cl (n=1), Ca-$HCO_3$ (n=10), Ca-$HCO_3$-Cl (n=1), Ca-$SO_4$ (n=2), Ca-Cl (n=2), Na-$HCO_3$ (n=1), Na-Cl-$HCO_3$ (n=2), and Na-Cl (n=1) (Table 1). These water types were then pooled into 3 major water groups, on the basis of inferred geochemical evolution history. Group 1 (n=13) corresponds to groundwater that has undergone relatively little geochemical evolution (including Mg-$HCO_3$-Cl, Ca-$HCO_3$ and Na-$HCO_3$ water types); TDS in this group is the lowest, varying between 96 and 349 mg/L with an average of 180 mg/L. Group 2 (n=3) represents more evolved groundwater, where carbonate dissolution and Ca-Na exchange have taken place, resulting in Na being the dominant cation, and Cl the dominant anion (Na-Cl-$HCO_3$ and Na-Cl water types). TDS in Group 2 samples vary between 213 and 556 mg/L, with an average of 350 mg/L. Finally, Group 3 (n=4) represents water with the most elevated salinity (water types Ca-SO$_4$ and Ca-Cl), with TDS between 537 and 1,975 mg/L, and an average of 1,304 mg/L (Table 1).

*Table 1. Details of the sampled residential (RES-XX) and observation (PO-XX) wells, including area, geology, distance to nearest producing O&G well, sampling depth, total dissolved solids (TDS), water type and assigned water group. Definition of water groups is explained in the text. Similar superscript symbols (¥, €, †, ‡) after the well ID indicate twin wells (e.g.: PO-01 and PO-14).*

| Well location and geological information | | | | | Major ion information | | |
|---|---|---|---|---|---|---|---|
| Well ID | Area | Geological Group | Distance to nearest producing O&G well (m) | Sampling depth (m) | TDS (mg/L) | Water type | Water group |
| RES-01 | McCully | Mabou | 378 | 20.7 | 186 | Ca-HCO$_3$ | 1 |
| RES-02 | McCully | Mabou | 288 | unknown | 128 | Ca-HCO$_3$ | 1 |
| RES-03 | Elgin | Mabou | 16,550 | unknown | 131 | Ca-HCO$_3$ | 1 |
| RES-04 | Elgin | Horton | 21,439 | 23.2 | 222 | Ca-HCO$_3$ | 1 |
| RES-05 | Elgin | Horton | 16,003 | 12.5 | 160 | Ca-HCO$_3$ | 1 |
| RES-06 | Elgin | Cumberland | 16,449 | 24.4 | 213 | Na-Cl-HCO$_3$ | 2 |
| RES-07 | Elgin | Sussex | 14,412 | 30.5 | 349 | Ca-HCO$_3$-Cl | 1 |
| PO-01$^{¥}$ | McCully | Mabou | 57 | 40 | 1,994 | Ca-SO$_4$ | 3 |
| PO-02$^{€}$ | McCully | Mabou | 54 | artesian | 537 | Ca-Cl | 3 |
| PO-03 | McCully | Mabou | 67 | 33 | 96 | Ca-HCO$_3$ | 1 |
| PO-04$^{\dagger}$ | McCully | Mabou | 45 | 18.4 | 245 | Ca-HCO$_3$ | 1 |
| PO-05 | McCully | Mabou | 54 | 16.5 | 98 | Mg-HCO$_3$-Cl | 1 |
| PO-06$^{\ddagger}$ | McCully | Mabou | 74 | 46 | 148 | Ca-HCO$_3$ | 1 |
| PO-07$^{\dagger}$ | McCully | Mabou | 50 | 17.5 | 241 | Ca-HCO$_3$ | 1 |
| PO-09$^{\ddagger}$ | McCully | Mabou | 74 | 45 | 155 | Ca-HCO$_3$ | 1 |
| PO-10 | Elgin | Mabou | 20,057 | 20 | 169 | Na-HCO$_3$ | 1 |
| PO-11 | Elgin | Mabou | 9,355 | 90 | 282 | Na-Cl-HCO$_3$ | 2 |
| PO-12 | Elgin | Horton | 16,090 | 23.2 | 556 | Na-Cl | 2 |
| PO-13$^{€}$ | McCully | Mabou | 56 | 49 | 710 | Ca-Cl | 3 |
| PO-14$^{¥}$ | McCully | Mabou | 59 | 49.7 | 1,975 | Ca-SO$_4$ | 3 |

Spatially, wells from Group 2 are only found in the Elgin area, and wells from Group 3 are exclusively found at the bottom of the Kennebecasis River valley in the McCully area. In contrast, wells from Group 1 are located throughout the whole study area (Table 1). Water groups were not found to be correlated with well depth, or with geology except for Group 3. Indeed, wells from Groups 1 and 2 are found among the four surficial geological units, namely the Cumberland, Mabou, Sussex and Horton groups (Table 1). Wells from Group 3 were all drilled within the Mabou Group, more precisely at the center of the Kennebecasis River valley which is known to host a buried diapir of Windsor Group marine evaporitic rocks. These underlying evaporites are composed of sulfates (anhydrite and gypsum), salt (halite), and potash (sylvinite), and have been mined for many years for potash deposits at the heart of the McCully gas field (Brake et al., 2019; Wilson et al., 2006).

Hence, the distribution of the three water groups is mainly governed by the hydrogeological context, where: 1) Group 1 represents recent recharge occurring throughout the whole study area due to local flow patterns; 2) Group 2 represents intermediately evolved water related to the less active aquifer parts in the Elgin area (the most plausible source of Cl in the Elgin area is the last marine transgression, which occurred some 10 000 years ago (Al et al., 2013); and 3) Group 3 represents the most chemically evolved water, which is likely related to deep regional flow discharging at the bottom of the Kennebecasis valley and entraining some salts from the buried diapir (Huchet, 2018).

## 5.2 Concentrations of methane and higher alkanes

Methane, ethane and propane concentrations were analyzed in all individual samples collected at each well, over the total study duration of 33 months. The number of samples collected per well varies between 1 and 10 (Table 2). For each well where more than one sample was collected, the geometric mean of concentrations was computed. For these calculations, non-detects were assigned half the detection limit. Of note, performing repeated sampling of wells in a study increases the likelihood of sporadic detection of very low alkane concentrations (often close to detection limit). While all detections must be considered, a unique detection (for instance of ethane) in a well, at a very low concentration (close to detection limit), does not bear the same weight on interpretation as a consistent detection over time at high concentrations. To take this into account, the interpretation of the presence or absence of alkanes in a well is here being inferred on the basis of “consistency”. To be considered “consistently detected” in a well, the geometric mean concentrations of an individual alkane ($C_1$, $C_2$ or $C_3$) in samples from a well must be above detection limit. For instance, in well PO-09 which was sampled 8 times, ethane was detected only once, at a concentration of 0.045 mg/L. Because it was not detected in any of the other samples from this well (hence 7 samples were assigned half the detection limit), the computed geometric mean is below detection limit. Hence, while ethane was detected once on PO-09, it is not considered to be “consistently present” in this well.

Based on this, methane was “consistently detected” in 8 wells, namely RES-03, RES-04, RES-05, RES-06, twin wells PO-04/PO-07, PO-11, and PO-12. Methane was also detected in the only sample collected from PO-14, at a very low concentration (0.009 mg/L). However, PO-14 is a twin well for PO-01, and methane was only detected in 1 out of 8 samples at PO-01 (0.123 mg/L). Methane is therefore not considered to be “consistently” detected at this location. The highest geometric mean methane concentration for a given well in this region is 13.01 mg/L (well PO-12), while the highest concentration measured in an individual sample, also from PO-12, is 20.35 mg/L (Table 2). However, the vast majority of the measured concentrations in the various wells are much lower (94% of the individual samples have less than 10 mg/L $CH_4$, and 83% have less than 1 mg/L; see Appendix A for full results). Therefore, all measured concentrations are well below the solubility of methane at atmospheric pressure and local groundwater temperature ($\sim$31 mg/L at $P_{atm}$ and 10 °C). Hence, based on findings of Molofsky et al. (2016), degassing during sampling is not expected to be major, and measured concentrations may be considered reasonably representative of true downhole concentrations. Of note, when considering all wells, no general seasonal pattern in methane concentrations could be identified. A certain seasonal pattern was observed in twin wells PO-04/PO-07 and will be discussed in section 6.2.2.

Ethane was detected at very low concentrations (<0.01 mg/L) in a few individual samples from wells RES-03, RES-04, RES-06, PO-04, and PO-07. However, it was below detection limit in the vast majority of individual samples from these wells, and the resulting geometric mean is also below detection limit; ethane is therefore not considered to be consistently present in these wells. In contrast, ethane was consistently detected in 3 other wells, namely RES-05, PO-11, and PO-12, which also correspond to the wells with the highest measured methane concentrations. Ethane concentrations in these wells reach up to 2.51 mg/L. Finally, propane was only consistentely detected in PO-12, at concentrations of up to 0.165 mg/L. PO-12 is the only well installed in Horton Group rocks.

*Table 2. Concentrations of dissolved inorganic carbon (DIC) and $C_1$-$C_3$ alkanes (methane, ethane, propane), and isotopic composition of DIC ($\delta^{13}C_{DIC}$) and methane ($\delta^{13}C_{CH4}$, $\delta^{2}H_{CH4}$) in wells of the McCully/Elgin region. For DIC, only one or very few measurements are available per well. Hence, one value per well is shown here (the latest one, if more than one are available), but full results are available in Appendix A. For alkanes, several samples per well were normally available, and results are shown here for the minimum (Min), geometric mean (Mean), and maximum (Max) values obtained at each well, with "n" representing the total number of individual values available at a given well for the different types of analyses, over the total period of the study (33 months). Similar superscript symbols (¥, €, †, ‡) after the well ID indicate twin wells.*

| Well information | | Concentration | | | | | | | | | | | Isotopic composition | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | DIC (mg/L) | $C_1$-$C_3$ *n*-alkanes | | | | | | | | | | Methane | | | | | | | |
| Well ID | Geological Group | | n | Methane (mg/L) | | | Ethane (mg/L) | | | Propane (mg/L) | | | DIC (‰ VPDB) | $\delta^{13}C_{CH4}$ (‰ VPDB) | | | | $\delta^{2}H_{CH4}$ (‰ VSMOW) | | |
| | | | | Min | Mean | Max | Min | Mean | Max | Min | Mean | Max | | n | Min | Mean | Max | n | Min | Mean | Max |
| RES-01 | Mabou | 20.6 | 4 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | -17.22 | 0 | - | - | - | - | - | - | - |
| RES-02 | Mabou | 20.1 | 4 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | -15.13 | 0 | - | - | - | - | - | - | - |
| RES-03 | Mabou | 23.2 | 9 | 0.03 | 0.18 | 0.88 | BDL | 0.002 | 0.01 | BDL | BDL | BDL | -11.65 | 7 | -74.1 | -72.1 | -69.9 | 6 | -249 | -239 | -232 |
| RES-04 | Horton | 45.8 | 9 | 0.01 | 0.03 | 0.81 | BDL | BDL | 0.004 | BDL | BDL | BDL | -10.65 | 3 | -74.2 | -73.3 | -72.3 | 3 | -204 | -189 | -173 |
| RES-05 | Horton | 32.6 | 7 | 2.71 | 4.06 | 5.65 | BDL | 0.083 | 0.25 | BDL | BDL | BDL | -14.03 | 7 | -63.8 | -60.2 | -58.8 | 7 | -239 | -232 | -218 |
| RES-06 | Cumberland | 18.0 | 6 | 0.44 | 1.55 | 2.93 | BDL | BDL | 0.007 | BDL | BDL | BDL | -17.73 | 6 | -53 | -51.3 | -47.8 | 6 | -197 | -164 | -137 |
| RES-07 | Sussex | 49.9 | 1 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | -13.58 | 0 | - | - | - | - | - | - | - |
| PO-01¥ | Mabou | 10.2 | 8 | BDL | BDL | 0.12 | BDL | BDL | BDL | BDL | BDL | BDL | -13.66 | 0 | - | - | - | - | - | - | - |
| PO-02€ | Mabou | 19.6 | 4 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | -14.74 | 0 | - | - | - | - | - | - | - |
| PO-03 | Mabou | 17.2 | 4 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | -16.74 | 0 | - | - | - | - | - | - | - |
| PO-04† | Mabou | 59.0 | 10 | BDL | 0.06 | 0.78 | BDL | BDL | 0.005 | BDL | BDL | BDL | -15.53 | 7 | -70.1 | -49.8 | -34.5 | 6 | -287 | -227 | -133 |
| PO-05 | Mabou | 19.5 | 4 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | -24.64 | 0 | - | - | - | - | - | - | - |
| PO-06‡ | Mabou | 34.0 | 6 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.005 | -17.30 | 0 | - | - | - | - | - | - | - |
| PO-07† | Mabou | 61.0 | 8 | BDL | 0.06 | 0.84 | BDL | BDL | 0.007 | BDL | BDL | BDL | -15.22 | 5 | -55.1 | -50.9 | -47.2 | 5 | -279 | -216 | -160 |
| PO-09‡ | Mabou | 33.4 | 8 | BDL | BDL | 0.02 | BDL | BDL | 0.045 | BDL | BDL | 0.009 | -16.70 | 0 | - | - | - | - | - | - | - |
| PO-10 | Mabou | 34.6 | 4 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.005 | -11.14 | 0 | - | - | - | - | - | - | - |
| PO-11 | Mabou | 23.6 | 4 | 10.75 | 12.25 | 15.57 | 0.01 | 0.016 | 0.022 | BDL | BDL | BDL | -12.84 | 4 | -62.9 | -61.8 | -59.8 | 4 | -265 | -246 | -226 |
| PO-12 | Horton | 70.1 | 3 | 6.73 | 13.01 | 20.35 | 1.4 | 2.51 | 3.65 | 0.011 | 0.031 | 0.165 | +18.01 | 3 | -61 | -56.7 | -53.5 | 3 | -257 | -248 | -234 |
| PO-13€ | Mabou | 17.2 | 1 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | -14.01 | 0 | - | - | - | - | - | - | - |
| PO-14¥ | Mabou | 11.1 | 1 | 0.01 | 0.01 | 0.01 | BDL | BDL | BDL | BDL | BDL | BDL | -14.42 | 0 | - | - | - | - | - | - | - |

BDL: below detection limit. Detection limit in this study is 0.006 mg/L for methane, 0.002 mg/L for ethane, and 0.01 for and propane.

## 5.3 Isotopic composition of methane

Methane isotopic composition ($\delta^{13}C_{CH4}$, $\delta^{2}H_{CH4}$) was analyzed in all samples that contained sufficient concentrations (Table 2). The geometric mean of isotopic values, calculated for each well, vary between -73.3 and -49.8‰ for $\delta^{13}C_{CH4}$, and between -248 and -164‰ for $\delta^{2}H_{CH4}$. When considering the whole pool of individual samples, values vary between -74.2 and -34.5‰ for $\delta^{13}C_{CH4}$, and between -279 and -133‰ for $\delta^{2}H_{CH4}$. Complete results are presented in Appendix A.

## 6 Interpretation of results

## 6.1 Factors controlling methane distribution

The methane concentrations for all samples were grouped into five classes, namely undetected (<0.006 mg/L), very low (0.006-1 mg/L), low (1-5 mg/L), moderate (5-20 mg/L), and high (>20 mg/L), which are shown on Fig. 3. High concentrations were only detected in one individual sample from PO-12, but the geometric mean of all samples in this well is 13.01 mg/L, hence considered “moderate”. Methane was seldom detected in the wells from the McCully gas field area, where all sampled water wells were located within either 75 m (observation wells) or 400 m (residential wells) of a producing unconventional gas well. Only 2 of the 13 wells in this area consistently had detectable methane (twin wells PO-04 and PO-07), and concentrations were always very low (< 1 mg/L; Fig. 3). In contrast, in the Elgin area, methane was consistently detected in 6 of the 7 wells, even though no hydrocarbon production and very little exploration has taken place in this area. In this case, concentrations varied widely between wells, ranging from undetected to high (<0.006 mg/L to 20.35 mg/L) in individual samples. These marked differences between the McCully and Elgin areas could be related, at least partly, to the fact that in the former, the hydrocarbon-bearing Horton Group rocks are found at >1,000 m depth below ground surface, whereas in the Elgin area, they outcrop at several locations and, elsewhere, are at shallow depths.

Methane concentrations indeed appear to be somewhat related to bedrock geology (Fig. 3). The wells completed into the Sussex, Cumberland and Mabou groups always had < 3mg/L methane, except for PO-11. This well is by far the deepest of all sampled wells (sampling depth of 90 m, total depth of 130 m), and the measured concentrations varied between 10.75 and 15.57 mg/L in individual samples (Table 1). While being drilled in the Mabou Group, PO-11 is located along a major fault, and Horton Group rocks are known to outcrop nearby (Fig. 3). Other wells drilled into the hydrocarbon-bearing Horton Group rock, or in unconsolidated sediments right above, tended to have the highest concentrations (up to 20.35 mg/L), although one of the wells (RES-04) rather exhibited very low concentrations (0.01-0.81 mg/L). Therefore, there seems to be a tendency for Horton group wells to exhibit higher methane concentrations compared to Sussex, Cumberland and Mabou group wells. No correlation with topography or proximity to gas well was observed.

Other factors which have previously been reported to favor the presence of methane include an evolved water type such as Na-$HCO_3$ or Na-Cl (McPhillips et al., 2014; Molofsky et al., 2013; Warner et al., 2012, among others), or low hydraulic conductivities and confined aquifer conditions (Bordeleau et al., 2018b). These factors are typically associated with longer groundwater residence time and anoxic conditions, which are favorable to microbial methanogenesis. However, in the McCully and Elgin areas, observation wells were determined to be under unconfined or semi-confined conditions (Huchet, 2018). Confinement conditions were not evaluated for residential wells, but are expected to be similar, as they were completed at similar depths and in similar rock units. Furthermore, hydraulic conductivities (K) of the bedrock aquifer, which were estimated from slug tests in wells PO-01, PO-03, PO-04, PO-05, PO-06, PO-07, and PO-10, show relatively good permeability, typically ranging from $10^{-6}$ to $10^{-4}$ m/s (Huchet, 2018). Among these, the only wells that do contain methane (PO-04 and PO-07) have K values of $1.6x10^{-5}$ and $1.1x10^{-5}$ m/s, respectively, thus being in the middle of this range. At the lower end of the range, we find well PO-10, with an estimated K of $9.4X10^{-7}$ m/s; none of the samples from this well contained methane at detectable concentrations. Therefore, confinement conditions and hydraulic conductivity do not seem to govern the presence of methane in this region.

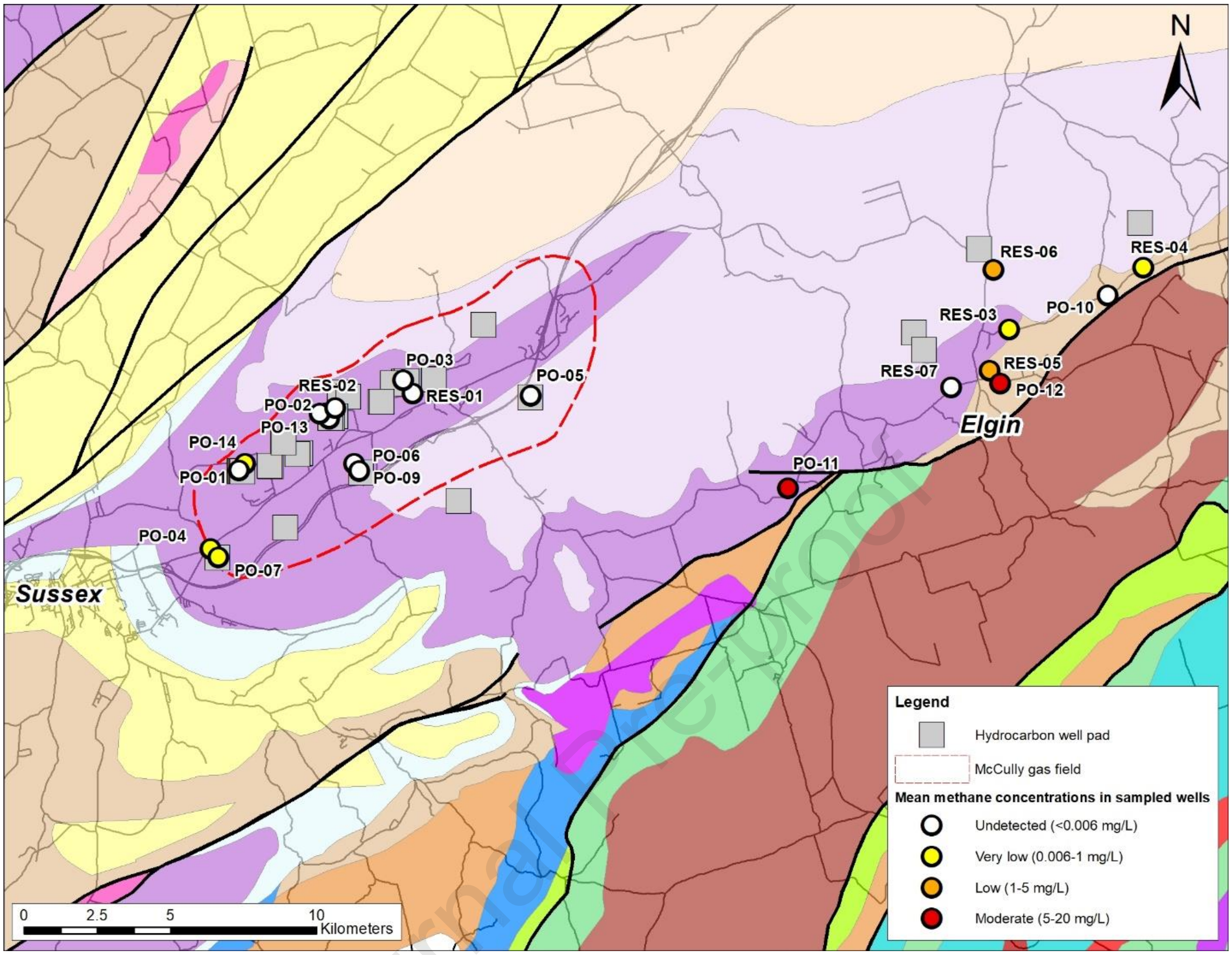

*Figure 3. Mean methane concentrations measured in samples from visited wells. Concentrations are grouped in 4 classes, namely: undetected (<0.006 mg/L, in white): very low (0.006-1 mg/L, in yellow), low (1-5 mg/L, in orange), and moderate (5-20 mg/L, in red). The class assigned to each well is based on the geometric mean methane concentration from all the individual samples collected at this given well. The class for "high concentrations" (>20 mg/L) mentioned in the text is not represented here, because concentrations above 20 mg/L were only measured in one individual sample from well PO-12, but the mean concentration for PO-12 remains within the "moderate" class. Bedrock geology is the same as on Fig. 1.*

The relationship between methane and water types was then evaluated. Not surprisingly, the most recently infiltrated waters forming water group 1 either did not contain detectable methane (most wells), or contained very low (0.006 - 1 mg/L) methane concentrations (twin wells PO-04/PO-07). One exception is well RES-05 (completed in unconsolidated sediment), which exhibited methane concentrations between 2.71 and 5.65 mg/L). This particular well will be discussed in section 6.2.3. Wells from water group 3, which have the highest salinities, also typically did not contain detectable methane (except for two individual samples from twin wells PO-01/PO-14, which contained concentrations of 0.12 and 0.01

mg/L). The highest methane concentrations were rather detected in samples from water group 2, which represents moderately evolved, Na-Cl waters, all of which are located in the Elgin area (Fig. 4).

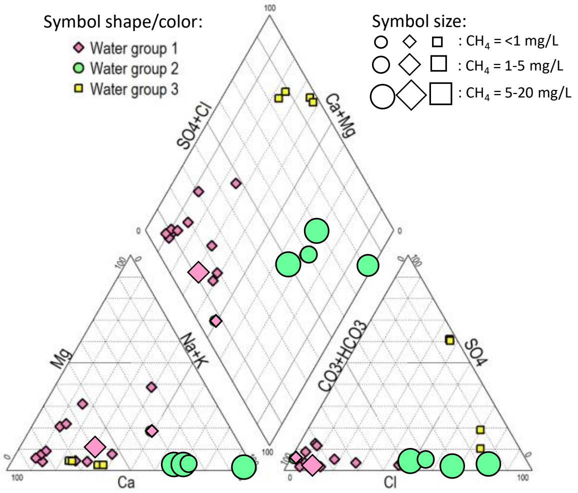

*Figure 4. Piper diagram of the groundwater sampled from wells in the study area. Wells are grouped (by symbol shape/color) according to the three main Water groups described in section 5.1. The size of the symbols represents classes of methane concentrations. For clarity, the lower two classes (<0.006 and 0.006-1 mg/L) which were presented on Fig. 3, were merged on the Piper diagram. Also, no mean methane concentration in any given well was within the "high" class (>20 mg/L). Consequently, the three classes used here correspond to: <1, 1-5, and 5-20 mg/L methane.*

## 6.2 Origin of methane and processes affecting its composition

As mentioned earlier, methane origin is typically determined using indicators such as the isotopic composition of methane and the gas dryness ratio, which corresponds to the molar concentrations of methane over ethane+propane ($[C_1]/[C_2+C_3]$). Indeed, methanogens are known to be able to produce only minimal amounts of $C_{2+}$ hydrocarbons (Tazaz et al., 2013), such that gas dryness ratios under 100 are usually considered indicative of thermogenic gas, while ratios above 1,000 are indicative of microbial gas (Golding et al., 2013 and authors therein). The well-known Bernard (1978) diagram, relating dryness ratio and $\delta^{13}C_{CH4}$, has commonly been used to infer gas origin. However, in an overwhelming number of samples throughout the literature, values fall outside of the genetic fields for microbial and thermogenic gas, which could indicate either mixing between gases of different origins, or processes affecting methane during or after its formation. Recently, the original Bernard diagram was updated using a comprehensive database of > 20 000 samples collected worldwide (Milkov and Etiope, 2018). Nonetheless, ambiguous methane origin occurs in the present study, like in many others, as nearly all of the sampled wells have some of their individual samples falling in different fields, or at the boundary of more than one field (Fig. 5). The only well whose samples falls completely within the microbial field is PO-11. Samples from RES-04 also fall entirely within the microbial domain in terms of $\delta^{13}C_{CH4}$, but their dryness ratios could not be quantified, as ethane and propane were not detected (Fig. 5).

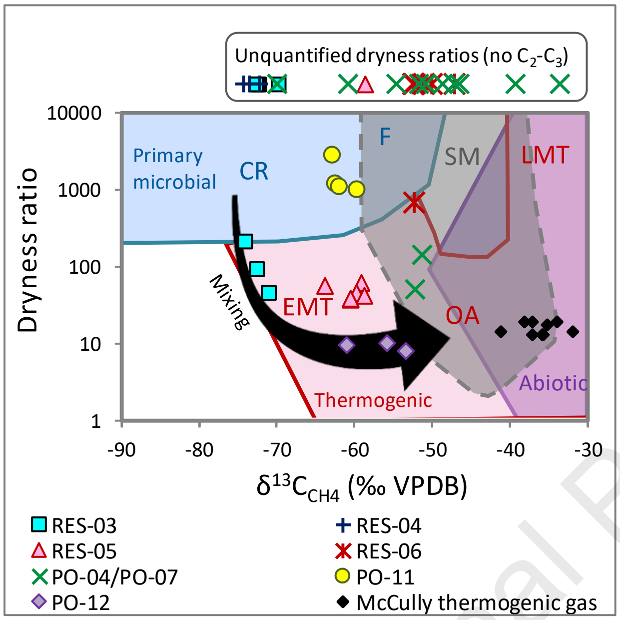

*Figure 5. Diagram of dryness ratio ($[C_1]/[C_2+C_3]$) versus methane carbon isotopic composition ($\delta^{13}C_{CH4}$), for all samples containing sufficient methane in the residential (RES-XX) and observation (PO-XX) wells. Samples containing methane ($C_1$) but no ethane ($C_2$) or propane ($C_3$) do not have a quantifiable dryness ratio, but their $\delta^{13}C_{CH4}$ values are shown within a box at the top of the graph. General fields for microbial gas (light blue), thermogenic gas (pink), secondary microbial gas (gray), and abiotic gas (purple) are from Milkov and Etiope (2018);. Within the primary microbial field, CR stands for "$CO_2$ reduction pathway", and F is "fermentation pathway". Within the thermogenic field, EMT is "early mature thermogenic" and LMT is "late mature thermogenic", and OA is "oil-associated". Lastly, SM stands for "secondary microbial". A general trend is shown to illustrate the effect of mixing between microbial and thermogenic gas (black arrow). Other processes can affect the dryness ratios and isotopic composition; these are more complex to model and are not shown on the figure, but are discussed in the following sections.*

These ambiguous values blur interpretations and make it impossible to identify the origin of the methane with a reasonable level of certainty. This issue is not trivial, as the central goal of most methane field studies is to detect the presence of thermogenic gas in shallow groundwater, which could potentially indicate contamination of aquifers with hydrocarbon gas originating from greater depths and possibly other undesirable compounds that could migrate upward either naturally, or as a result of hydrocarbon-related activities. It is therefore crucial to be able to unequivocally identify the presence of thermogenic gas in groundwater, i.e. distinguish it from microbial gas whose chemical signature could have been modified through different processes.

In order to resolve the gas origin for the McCully-Elgin wells, four processes have been investigated that could be responsible for the intermediate isotopic values and dryness ratios observed on Figure 5. These processes include: 1) late-stage microbial methanogenesis, 2) hydrocarbon oxidation, 3) mixing between microbial and thermogenic gas, and 4) secondary methanogenesis. The first process involves only microbial gas, while the second could involve microbial or thermogenic gas, and the last two processes necessarily involve the presence of thermogenic gas.

### 6.2.1 Late-stage methanogenesis

Late-stage methanogenesis refers to microbial methane that is produced from a limited carbon ($CO_2$ or acetate) reservoir, which becomes increasingly exhausted over time; the resulting isotopic effect leads to the formation of microbial gas with high $\delta^{13}C_{CH4}$ values that could otherwise seem typical of thermogenic gas. Indeed, when converting carbon substrates to methane, methanogens preferentially use isotopically light ($^{12}C$) atoms, leaving a larger proportion of heavy ($^{13}C$) atoms in the remaining reactant pool (Whiticar, 1999). Generally, in parts of the aquifer with active groundwater flow, recharge will bring in fresh carbon, and the isotopic composition of the substrate (acetate or $CO_2$, the latter being a component of DIC) and product ($CH_4$) pools may not be perceptibly affected over time. The resulting carbon isotopic composition of the reactant remains typical of its usual composition under the local environmental conditions (see below for discussion on DIC), and the isotopic composition of the produced methane is typical of microbial gas formed via one of the two methanogenic pathways.

In contrast, when methanogenesis occurs in a closed or nearly closed carbon reservoir, substrate depletion may occur. In this case, the kinetic isotope effects will cause the isotopic composition of both the substrate and the product to gradually increase, eventually resulting in what is called "late-stage methanogenesis", where $\delta^{13}C_{DIC}$ and $\delta^{13}C_{CH4}$ are significantly higher than expected for microbial gas. Any $\delta^{13}C_{DIC}$ value above 0‰ is considered related to late-stage methanogenesis, and values as high as +32‰ $\delta^{13}C_{DIC}$, and -40‰ $\delta^{13}C_{CH4}$ have been reported (Golding et al., 2013; Jones et al., 2008; Kotelnikova, 2002; Martini et al., 1998; Rivard et al., 2018). This Rayleigh effect is not observed on the $\delta^{2}H_{CH4}$ of methane formed via the $CO_2$ reduction pathway, as the hydrogen molecules come from the ambient water (Balabane et al., 1987; Daniels et al., 1980), which is in comparatively unlimited supply, hence no hydrogen reservoir depletion occurs. For methane formed via the aceticlastic pathway, where hydrogen comes from the acetate pool, this Rayleigh effect on the $\delta^2H_{CH4}$ could potentially be observed to some extent (as reservoir depletion could occur in the acetate pool), although to our knowledge it has never been documented. However, hydrogen exchange between groundwater, acetate and methane do occur (Balabane et al., 1987; De Graaf et al., 1996; Waldron et al., 1999), which complicates estimation of the evolution of $\delta^2H_{CH4}$ if the acetate pool was to be depleted. Hence, late-stage methanogenesis will be investigated from the carbon isotopic composition only. To do so, it is first necessary to estimate the expected "normal" range of isotopic values for DIC ($\delta^{13}C_{DIC}$) and microbial methane ($\delta^{13}C_{CH4}$) in a given aquifer, and then to model the expected isotopic trend related to reservoir depletion.

Computing a "normal" $\delta^{13}C_{DIC}$ range in groundwater is achieved by considering the locally relevant sources of DIC, which may include: 1) soil $CO_2$, 2) pedogenic carbonates, 3) marine carbonates, and 4) possibly oxidation of fossil hydrocarbon, in the case of hydrocarbon-bearing host rocks. Both soil $CO_2$ and pedogenic carbonates originating from the decay of modern C3 plants, which are estimated to make up more than 95% of plants in eastern Canada and other areas with temperate climates (Still et al., 2003), have $\delta^{13}C_{DIC}$ around -23 to -27‰. In contrast, marine carbonates have $\delta^{13}C_{DIC}$ values ≈ 0‰ (Clark and Fritz, 1997). Groundwater circulating in marine carbonate-bearing formations is thus expected to evolve from an original $\delta^{13}C_{DIC}$ value that could be as low as -27‰, towards carbonate-influenced final $\delta^{13}C_{DIC}$ values around -11 to -16‰ (Clark and Fritz, 1997; Sharma et al., 2013). In non-marine carbonate-bearing formations, the $\delta^{13}C_{DIC}$ values should remain closer to soil $CO_2$ values, i.e. -23 to -27‰. In the present study area, marine carbonates are scarce. They are thought to be present only in the Windsor Group (which underlies the Mabou Group in the McCully gas field), and in rocks of the Albert Formation (deposited in a lacustrine environment but having undergone a few marine incursions), which outcrop in the Elgin area. Hence, in the study area, $\delta^{13}C_{DIC}$ values covering the full range related to soil $CO_2$, marine and pedogenic carbonates (-27 to -11‰) could be expected. As for oxidation of fossil hydrocarbons, it could only occur in Horton Group rocks, which are known to host thermogenic hydrocarbons with $\delta^{13}C_{CH4}$, $\delta^{13}C_{C2H6}$ and $\delta^{13}C_{C3H8}$ values between -15 and -41‰ (Al et al., 2013; Barton, 2018). If oxidation of these hydrocarbons occurred, at the onset of the process, the produced DIC would have a $\delta^{13}C$ value more negative than the parent hydrocarbons. As oxidation progresses, the $\delta^{13}C_{DIC}$ values of the newly-formed DIC pool would gradually increase, eventually reaching the original value of the parent hydrocarbons once degradation is complete. Therefore, the $\delta^{13}C$ of the DIC pool produced from fossil hydrocarbon oxidation, at any stage of the process, would be more negative than, or similar to, the $\delta^{13}C$ of the (expectedly more ubiquitous) DIC coming from soil $CO_2$ or carbonates. At the same time, the $\delta^{13}C$ values of the residual (non-oxidized) hydrocarbons would increase. In the range of values reported by Al et al. (2013) for gas from Horton Group rocks, all wells tapping the Hiram Brook sandstone have hydrocarbon $\delta^{13}C$ values typical of thermogenic gas, while wells (F58 and M66) tapping the Frederick Brook shale have unusually enriched $\delta^{13}C_{CH4}$ values that could indicate partial oxidation. Nonetheless, here we must consider that: 1) the Frederick Brook shale in the McCully area is found only at depths greater than 1.7 km (Brake et al., 2019; Séjourné, 2017); 2) Horton Group rocks do occur near the surface in the Elgin area (Fig. 1); but 3) none of the shallow groundwater samples in the whole study area had $\delta^{13}C_{DIC}$ values more negative than what would be expected from soil $CO_2$ and carbonates. Consequently, a DIC source related to fossil hydrocarbon oxidation (which could theoretically produce very $^{13}C$-depleted DIC) does not need to be considered in our model (see below), and the range of expected $\delta^{13}C_{DIC}$ values is limited to those coming from soil $CO_2$ and carbonates (-27 to -11‰).

Considering this range , it is then possible to estimate $\delta^{13}C_{CH4}$ values for microbial methane formed via $CO_2$ reduction and acetate fermentation, based on published fractionation factors (α) or enrichment factors (ε) (Eq. 1; Whiticar, 1999).

$$\varepsilon \approx 10^3 \ln(\alpha) \approx 10^3(\alpha - 1) \approx \delta^{13}C_{DIC} - \delta^{13}C_{CH4} \qquad \text{Eq.1}$$

Several fractionation factors for methanogenesis have been published, either from laboratory cultures, or from natural observations (Whiticar, 1999). For the $CO_2$ reduction pathway, most enrichment factors vary between approximately 1.057 and 1.078, corresponding to enrichment factors (ε) between 55 and 75‰ (Whiticar, 1999 and authors therein). For methyl-type fermentation, fractionation factors observed under natural conditions typically vary between 1.041 and 1.057, corresponding to ε between 40 and 55‰ (Whiticar, 1999). Based on Eq. 1, the resulting microbial $\delta^{13}C_{CH4}$ values in the McCully-Elgin region should be between -51 and -82‰ (methyl-type fermentation), and between -66 and -102‰ ($CO_2$ reduction). This is in agreement with the usual range of microbial $\delta^{13}C_{CH4}$ values typically reported in the scientific literature, although the lower end of the range (below ≈ -85‰) is rarely observed. In the McCully-Elgin wells, the actual lowest $\delta^{13}C_{CH4}$ values are around -74‰.

Considering the local ranges of $\delta^{13}C_{DIC}$ and $\delta^{13}C_{CH4}$ values, a trend for late-stage methanogenesis can then be modeled using Rayleigh equations for the evolution of $\delta^{13}C$ values in a completely closed reservoir:

$$\mathrm{R_{r,t}} = \mathrm{R_{r,i}} \cdot f^{(\alpha^{*}-1)} \qquad \text{Eq. 3}$$

$$\mathrm{R_{p,t}} = \mathrm{R_{r,i}} \left(\frac{1-f^{\alpha^{*}}}{1-f}\right) \qquad \text{Eq. 4}$$

Where R is the isotope ratio ($^{13}C/^{12}C$) of the reactant (r) or product (p) at time $t$ or initially (i), $f$ is the fraction of initial substrate remaining at time $t$, and α* is the reciprocal kinetic isotope fractionation factor. Fractionation factors are usually provided in values larger than 1. In Eq. 3 and 4, to account for the fact that the $\delta^{13}C$ in the reactant pool becomes progressively heavier, the reciprocal of α (α*= 1/α) must be used (Kendall and Caldwell, 1998).

In practice, the reactant reservoir in the aquifer may not be perfectly closed, but rather highly restricted, with minor additions of fresh DIC. The isotopic evolution of the reactant and product may then deviate somewhat from the computed trends, but it remains that elevated $\delta^{13}C_{DIC}$ and $\delta^{13}C_{CH4}$ values will be highly indicative of late-stage methanogenesis.

For the McCully-Elgin region, samples from most wells have $\delta^{13}C_{DIC}$ that fit within the expected range of "normal" $\delta^{13}C_{DIC}$ (see Table 2 for results at all wells, and Fig. 6 for the sub-set of wells containing enough methane to allow isotopic analyses). The modeled trend of reservoir depletion, which represents late-stage methanogenesis, is shown as a grey arrow on Fig. 6. This process is not ubiquitous in this region, as only samples from well PO-12 could fit this trend. This well is indeed completed into black shale and likely has unfractured strata that act as a confining layer, impeding direct recharge. It has a very low yield and contains Na-Cl water, hence an evolved water type which could be consistent with conditions necessary for late-stage methanogenesis. However, samples from PO-12 also have the highest ethane and propane concentrations of our dataset (dryness ratios between 8 and 10), which cannot be explained by late-stage methanogenesis. This indicates that other processes affect the water in this well (see sections 6.2.3 and 6.2.4). Also, samples from wells RES-06 and twin wells PO-04/PO-07 plot outside of the expected local range of $\delta^{13}C_{DIC}$ and $\delta^{13}C_{CH4}$ values, but cannot be explained by late-stage methanogenesis (Fig. 6). These samples will be discussed in section 6.2.2.

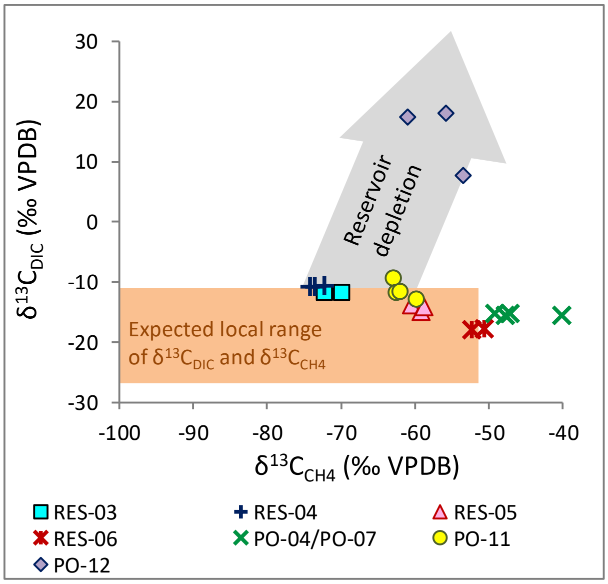

*Figure 6. Isotopic composition of methane ($\delta^{13}C_{CH4}$) and DIC ($\delta^{13}C_{DIC}$) in the McCully-Elgin groundwater samples. All values available for a given well over the study period are presented here (see Appendix A for detailed results). The orange band represents the expected range of values for regular DIC and regular (non late-stage) microbial methane in this region. The gray arrow represents the isotopic trend resulting from progressive reservoir depletion, i.e. late-stage methanogenesis.*

### 6.2.2 Oxidation

Microbial oxidation is a process through which methane or higher hydrocarbons are converted to $CO_2$ or $HCO_3$. Due to kinetic fractionation, the $\delta^{13}C$ and $\delta^2H$ compositions of the hydrocarbon species being oxidized gradually increase in the residual hydrocarbon pool (Alperin et al., 1988; Kinnaman et al., 2007; Kotelnikova, 2002; Mastalerz et al., 2009).

Under aerobic conditions, higher hydrocarbons (e.g. ethane and propane) are being preferentially oxidized over methane (Kinnaman et al., 2007). For aerobic oxidation of thermogenic gas, this would result in a constantly increasing dryness ratio, eventually resembling dryness ratios reminiscent of microbial gas. This could explain a few of the values from twin wells PO-04/PO-07 that plot high above the thermogenic gas domain (Fig. 5); however, most samples from PO-04/PO-07 have $\delta^{13}C_{CH4}$ values typical of microbial gas, which is not consistent with thermogenic gas aerobic oxidation; this process is therefore not considered as the most likely process for these wells.

In contrast, under anaerobic conditions, methane is usually being preferentially oxidized over ethane (Mastalerz et al., 2009; Whiticar, 1999). Non-methane hydrocarbons like propane (Kniemeyer et al., 2007; Mastalerz et al., 2009), butane (Kniemeyer et al., 2007), and oil (Formolo et al., 2004; Joye et al., 2004; based on isotopic data from Kennicutt et al., 1985), were shown to sometimes be oxidized by sulfate-reducing bacteria under anoxic conditions in marine hydrocarbon seeps. Nonetheless, anaerobic oxidation was generally reported as leading to a decrease in dryness ratio, with observed ratios as low as 10 (i.e. otherwise typical of thermogenic gas Whiticar, 1999). Of course, a decrease in the dryness ratio will not be noticeable in samples where ethane and propane concentrations are below detection limit. Hence, samples with high $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$ values, and possibly (but not necessarily) low dryness ratio, could indicate microbial methane that has been partially oxidized under anoxic conditions, rather than thermogenic gas as it would normally be interpreted. However, anaerobically-oxidized microbial methane can be distinguished from thermogenic methane by comparing $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$ values, knowing the specific fractionation factors associated with the C and H atoms in the $CH_4$ molecule (Alperin et al., 1988; Grossman et al., 2002; King et al., 1989; Kinnaman et al., 2007; Tyler et al., 1994; Whiticar, 1999). This approach is particularly powerful when multiple samples are available for a given well, considering that various extents of oxidation can occur in a well over time, leading to predictable patterns in $\delta^{13}C_{CH4}$ versus $\delta^{2}H_{CH4}$ values.

In order to model such general oxidation patterns for a given region, it is first necessary to determine the expected isotopic values for non-oxidized microbial gas. Local expected microbial $\delta^{13}C_{CH4}$ values have been discussed above (section 6.2.1). The expected site-specific $\delta^{2}H_{CH4}$ values can be computed using local groundwater hydrogen isotopic values ($\delta^{2}H_{H2O}$), considering isotopic equations for fractionation between a single substrate and product. However, for hydrogen, an approximation such as in Equation 1 should not be used (Sessions and Hayes, 2005). Indeed, such approximation is considered reasonably accurate for isotopes like those of carbon or oxygen, where fractionation factors (α) approach unity (typically varying between 0.95 and 1.05), but not for isotopes with larger fractionation like hydrogen with α commonly varying from 0.7 to 1.5. In this case, the following equation must be used (see Sessions and Hayes, 2005, for full derivation):

$$\delta_P = \alpha\delta_S + \varepsilon \qquad \text{Eq. 4}$$

where values are not expressed in per mil (i.e. any values in ‰ should be divided by 1000), $\delta_P$ and $\delta_S$ are the delta values of the product and substrate, respectively, and $\varepsilon = \alpha - 1$.

For the $CO_2$ reduction pathway, considering the documented ε values (Golding et al., 2013; Whiticar, 1999), the $\delta^2H$ of the produced methane can be calculated from Equation 4.

$CO_2$ reduction: $\delta^2H_{CH4}$ (‰) = $0.84(\pm0.01)*\delta^2H_{H2O}$ -160(±10) Eq. 4

For methane formed via the aceticlastic pathway, a linear relationship resembling that of Eq. 4 was derived from a regression performed on samples collected in various natural freshwater environments (Waldron et al., 1999). However, the authors note that values of the slope (α) and the intercept (ε) do not follow the usual relationship (ε = α-1), possibly due to microbial processes which induce post-genetic hydrogen exchange between methane and groundwater. Nonetheless, the equation determined from the linear regression is the following:

Acetate fermentation: $\delta^2H_{CH4}$ (‰) = 0.675 $\delta^2H_{H2O}$ -284 (±6) (Waldron et al., 1999) Eq. 5

Considering equations 4 and 5, and the range of measured $\delta^2H_{H2O}$ values in the McCully-Elgin samples (-76 to -62‰; see Appendix A), the original (i.e. non-oxidized) microbial $\delta^2H_{CH4}$ values should be between -203 and -233‰ for $CH_4$ formed via $CO_2$ reduction, and between -320 and -341‰ for $CH_4$ formed via acetate fermentation (green and orange rectangles, respectively, on Fig. 7).

Based on this original (non-oxidized) microbial methane isotopic composition, the isotopic effect of progressive oxidation on the residual methane pool can be modeled through Rayleigh distillation (Eq. 3). Several fractionation factors (ε) for anaerobic oxidation were used, based on those documented in the literature. For carbon, they include: -8.8‰ (average factor from Alperin et al., 1988), -29‰ (average factor from Kinnaman et al., 2007), -4 and -20‰ (minimum and maximum factors from Whiticar, 1999). For hydrogen, they range from -157‰ (average factor fromAlperin et al., 1988) to -238‰ (average factor from Kinnaman et al., 2007).

For each original microbial methane pool ($CO_2$ reduction and acetate fermentation; green and orange rectangles on Fig. 7), using various fractionation factors results in linear trends that originate from the original pool and progress at a different angle depending on the magnitude of α. Hence, the range of linear trends widens as it progresses away from the original microbial methane pool (green and orange arrows on Fig. 7). The sub-horizontal trends demonstrate that during oxidation, the magnitude of variations is higher on $\delta^2H_{CH4}$ than for $\delta^{13}C_{CH4}$.

Samples from residential well RES-06 and twin observation wells PO-04/PO-07 align very well along the oxidation trend for microbial methane formed via acetate fermentation. If these variations were due to mixing between thermogenic and microbial gas, the most $^{2}$H- and $^{13}$C-enriched samples in a given well should be the ones containing the highest proportion of thermogenic gas (i.e. containing more $C_{2+}$ hydrocarbons). However, the two individual samples from these wells which do contain a small amount of ethane (< 0.007 mg/L) fall towards the middle of the wells' range of isotopic values, and are therefore not the most $^{2}$H- and $^{13}$C-enriched samples from these given wells. Moreover, when modelling a simple mixing between a microbial end-member (represented by the most $^{13}$C- and $^{2}$H-depleted sample from PO-04/PO-07) and the documented range of isotopic values in Horton Group thermogenic gas from the McCully gas field ($\delta^{13}C_{CH4}$ between -38 and -19‰, with corresponding $\delta^{2}H_{CH4}$ values of -72 and -128‰, respectively; Al et al., 2013), we find that the isotopic composition of the samples from PO-04 and PO-07 do not match the modelled mixing trends (not shown). Hence, mixing between microbial and thermogenic gas is not considered as the most likely process governing the isotopic values of methane in these wells.

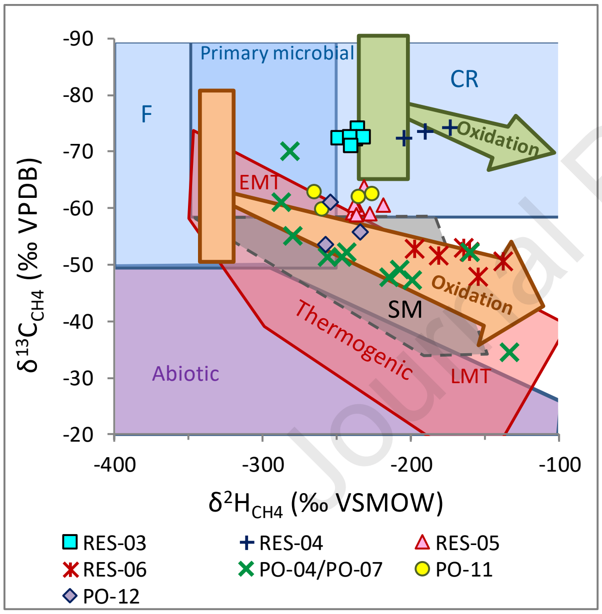

*Figure 7. Methane hydrogen ($\delta^{2}H_{CH4}$) versus carbon ($\delta^{13}C_{CH4}$) isotopic composition. Fields for primary microbial gas (light blue), thermogenic gas (pink), secondary microbial gas (gray) and abiotic gas (purple) are based on Milkov and Etiope (2018), who have updated the original fields defined by Whiticar (1999) with a dataset comprising >20 000 samples. Within these fields, F stands for "fermentation", CR is "$CO_2$ reduction", SM is "secondary methanogenesis", LMT is "late mature thermogenic", and EMT is "early mature thermogenic". The orange and green rectangles represent the composition of microbial gas (non-oxidized) formed in the McCully-Elgin region through acetate fermentation or $CO_2$ reduction, respectively. The orange and green arrows represent the anaerobic oxidation trends for microbial gas formed in this region via both methanogenic pathways. Calculations for the rectangles and arrows are discussed in the text.*

In fact, the usual absence and occasional presence of ethane in samples from PO-04/PO-07 can be explained by different extents of oxidation and dilution. To begin with, redox potential (Eh) measured in-situ within these twin wells varied between +80 and +360 mV, which is not favorable to methanogenesis (Conrad, 2020; Whiticar, 1999), and suggests that the gas was formed somewhat deeper in the aquifer and migrated upwards, eventually reaching the wells. The dissolved oxygen (DO) concentrations measured in these wells varied largely over time (0.0-5.8 mg/L), which suggests variable groundwater recharge and/or sourcing of water from different horizons, which can both affect the amount of dilution and/or oxidation that methane undergoes. This phenomenon was also observed by Loomer et al. (2018) in wells of this region, where methane concentrations and major ion chemistry were shown to vary over time, especially in wells displaying several, low-yield water-bearing horizons. In such wells, sourcing of water from the different horizons during sampling can occur depending on factors such as water table depth, pumping rate, aquifer permeability and variable groundwater recharge. In wells PO-04/PO-07, we observe a seasonal effect on both methane and DO concentrations (Fig. 8), with peaks in methane accompanied by low DO in summer samples (August 2016, June 2017, June 2018) when precipitations are lowest (Environment Canada, 2021). Inversely, dips in methane concentrations accompanied by peaks in DO are mostly observed in the spring (March 2016, March 2017) when snow melts, or in late fall (e.g. November 2016) when precipitations are most abundant (Environment Canada, 2021). The snowmelt and abundant fall precipitation can infiltrate fresh oxic, methane-free water in the aquifer, which could dilute in situ methane concentrations and possibly cause oxidation (preferentially of higher alkanes if present, then possibly also of methane). Unfortunately, seasonal variations in methane isotopic composition cannot be discerned from this dataset, as the samples with low concentrations (the "dips" on Fig. 8) did not contain sufficient methane to allow isotopic analyses. Nonetheless, it is clear that dilution alone could possibly explain the observed variations in methane concentrations, but not the observed high variations in isotopic composition in these wells, as dilution does not induce fractionation. Hence, we postulate a combined effect of dilution and oxidation to explain the variable methane concentrations (Fig. 8), and the systematic variations in $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$ (Fig. 7).

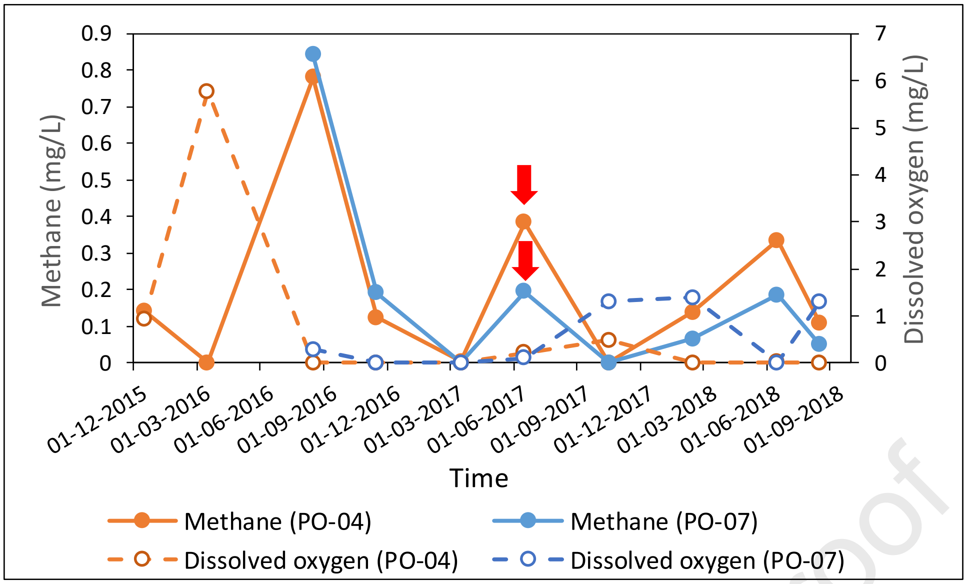

*Figure 8. Variations in concentrations (mg/L) of methane and dissolved oxygen (DO) over time in samples from twin shallow observation wells PO-04 and PO-07 (located in the McCully gas field), over the 33-month study period. Samples pointed by red arrows are the only two samples where ethane (<0.007 mg/L) was detected. Propane was never detected in samples from these wells.*

### 6.2.3 Mixing between thermogenic and microbial methane

The presence of thermogenic gas in samples was first assessed based on the detection of ethane and/or propane. The only wells which consistently contained measurable $C_{2+}$ hydrocarbons and dryness ratios lower than 100 are RES-05 and PO-12. These two wells are located in the Elgin area, on the same residential lot but at different depths: RES-05 is 12.5 m deep and installed in unconsolidated sediments, while PO-12 is 50 m deep and completed within hydrocarbon-bearing Horton Group bedrock. The measured $CH_4$ concentrations in PO-12 were always moderate to high (6.73-20.35 mg/L), and the $C_{2+}$ concentrations were the highest among all wells (up to 3.65 mg/L $C_2H_6$ and 0.17 mg/L $C_3H_8$). This yielded dryness ratios between 8 and 10, which unequivocally indicates the presence of (at least some) thermogenic gas. In residential well RES-05, $CH_4$ and $C_2H_6$ concentrations were comparatively lower, and while $C_2H_6$ was present in most samples, $C_3H_8$ was never detected. Dryness ratios varied between 38 and 64, except for one sample where $C_{2+}$ were not detected. While RES-05 is completed in the granular aquifer, it sits just 2.5 m above bedrock, hence it is likely that the underlying thermogenic gas migrates upwards into the granular aquifer, and possibly mixes with in situ microbial gas. This interpretation is supported by isotopic values, which suggest that both PO-12 and RES-05 contain predominantly thermogenic gas mixed with some microbial gas (Fig. 5).

The only other well with consistently detected ethane is PO-11, but with dryness ratios always above 1000 and $\delta^{13}C_{CH4}$ values well into the microbial field (Fig. 5); the gas in this well is thus considered to be microbial. A few other wells had measurable (but very low) ethane concentrations in a small number of their individual samples (RES-03, RES-06, PO-04, PO-07). The gas in RES-06, PO-04 and PO-07 was previously shown to be microbial gas undergoing oxidation. This is not the case for RES-03, which does not follow an oxidation trend (Fig. 7), but rather seems to exhibit mixing between thermogenic and microbial gas (Fig. 5). However, the samples containing ethane in RES-03 contained very low methane (0.029-0.51 mg/L), so it is difficult to draw firm conclusions.

### 6.2.4 Secondary methanogenesis

Secondary methanogenesis is another process that could involve the initial presence of thermogenic gas. In this case, methane or higher hydrocarbons in natural gas (or condensates) are biodegraded to $CO_2$ (via oxidation, under oxic or anoxic conditions) or acetate (via fermentation under anoxic conditions). When hydrocarbon biodegradation occurs in an anoxic environment, or when it occurs in oxic conditions but the water then migrates into a part of the aquifer with anoxic conditions, the newly-formed $CO_2$ or acetate can be used by methanogens to produce new (secondary) methane (Jautzy et al., 2021; Scott et al., 1994). For clarity, here we will only discuss degradation of hydrocarbons through oxidation into $CO_2$, but the same general principles could apply for hydrocarbon fermentation into acetate.

In groundwater studies, being able to detect secondary methanogenesis is highly relevant, as “apparent microbial gas” could in fact hide the presence of precursor thermogenic gas, and therefore potentially mask fugitive gas from O&G wells. Indeed, as discussed in section 6.2.2, the effect of hydrocarbon oxidation on gas dryness and isotopic composition will depend on whether the process is aerobic or anaerobic. Under anaerobic conditions, methane will typically be preferentially oxidized, and the produced $CO_2$ can then be turned back into secondary methane by methanogens (Mastalerz et al., 2009; Whiticar, 1999). Hence, as long as the secondary methanogenesis process is complete, there is no volumetric change in methane, so the dryness ratio and isotopic composition of the gas will be unchanged. And, regardless of whether the process is complete or not, secondary methanogenesis under anaerobic conditions would likely not mask the presence of thermogenic gas, as the $C_{2+}$ hydrocarbons are mostly recalcitrant to degradation under those conditions (Mastalerz et al., 2009). However, as observed in marine seep sediments, anaerobic sulfate reduction paired with hydrocarbon oxidation could degrade heavier hydrocarbons preferentially to methane; when doing so, sulfate-reducing bacteria utilize propane and/or n-butane as an energy source to reduce sulfate to sulfide (Kniemeyer et al., 2007). In the present study, sulfate was detected in groundwater of all wells except RES-05, and sulfides were below detection limit (<0.02 mg/L) in all wells except RES-06 (1.8 mg/L) and PO-12 (0.041 mg/L). Also, Eh and pH values measured in groundwater are mostly consistent with the stability of sulfate rather than sulfides (Grasby et al., 2003). Hence, sulfate-dependent anaerobic oxidation of propane or butane is not expected here.

In contrast, under aerobic conditions, higher hydrocarbons will be preferentially oxidized (Kinnaman et al., 2007). As a result, the gas dryness ratio will greatly increase, and could eventually resemble microbial gas. Also, as oxidation discriminates against heavy ($^{13}C$ and $^{2}H$) isotopes, the produced $CO_2$ will be highly $^{13}C$- and $^{2}H$-depleted at the beginning of degradation, and will gradually become less depleted. In a completely closed system, once $C_{2+}$ oxidation is complete, the $C_{2+}$ hydrocarbons will have imparted their original isotopic composition onto the produced $CO_2$. As $C_{2+}$ alkanes such as ethane, propane and butane ($C_2$-$C_4$) typically have $\delta^{13}C$ values in the order of approximately -35 to -20‰ (Rooney et al., 1995), the resulting $CO_2$ composition (upon complete $C_2$-$C_4$ oxidation) would greatly resemble the rest of the non-hydrocarbon related pool containing $CO_2$ from the soil and from pedogenic carbonates. In an open system however, as the oxidation progresses, values that are significantly more $^{13}C$-enriched could be observed in the produced $CO_2$, compared to a closed system. In any case however, in order for the newly-produced $CO_2$ to be reduced to secondary methane, it would need to migrate towards a portion of the aquifer where conditions are anoxic. Of note, if the oxidation and/or secondary methanogenesis reactions are incomplete, the gas dryness ratio would invariably increase, but the effect on the isotopic composition of methane would be more complex, and would depend on: 1) the hydrocarbon species that are oxidized, 2) the extent of hydrocarbon oxidation, and 3) the extent of secondary methanogenesis from the resulting $CO_2$ pool (Whyte et al., 2021).

Based on the reasons discussed above, in aquifers such as those in the McCully/Elgin region (i.e. mostly open-system conditions, with spatial and temporal variations in oxic/anoxic conditions), it is utterly difficult to identify the occurrence of secondary methanogenesis, unless the presence of $C_{2+}$ hydrocarbons and clear evidence of their oxidation (based on $C_{2+}$ isotopic data) are found. Among wells from this study, only PO-12 and RES-05 would have had sufficiently high ethane concentrations to allow isotopic analyses; unfortunately, these were not done. Also, the elevated $\delta^{13}C_{DIC}$ (which implies elevated $\delta^{13}C_{CO2}$) in samples from PO-12 were interpreted earlier (section 6.2.1) as indicating late-stage (primary) methanogenesis, but it could also support late-stage secondary methanogenesis. However, PO-12 and RES-05 clearly do contain some thermogenic gas along with some microbial gas, hence determining whether the microbial gas portion is primary or secondary microbial is not crucial for the purpose of an environmental study. In contrast, for other wells such as PO-04/PO-07 which are located directly on a gas well pad and where small concentrations of ethane were only detected once, it is very important to determine whether the gas is microbial or thermogenic. In these wells, the oxidizing conditions that were observed could support the first part of the process (preferential $C_{2+}$ hydrocarbon biodegradation), but not the second part (microbial methanogenesis from the newly-produced $CO_2$). Hence, based on redox conditions and on the observed systematic variations in $\delta^{13}C_{CH4}$ versus $\delta^{2}H_{CH4}$ (Fig. 7), we conclude that the gas in PO-04/PO-07 is most likely primary microbial gas that has been oxidized to various extents.

### 6.2.5 Integrating all processes

While initial interpretation of gas geochemical results (dryness ratio, $\delta^{13}C_{CH4}$) appeared ambiguous in most wells (Fig. 5), specific hints in the dataset (e.g. elevated $\delta^{13}C_{DIC}$, or co-variation of $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$ in time series samples from some wells; Fig. 7) prompted a thorough investigation of four processes that can alter the gas geochemical characteristics. Doing so allowed the unraveling of gas origin and identification of the processes that affected its composition (Table 3).

Results showed that in the McCully gas field area, the sampled wells contained either no hydrocarbons (most wells), or very low concentrations of methane and sometimes ethane (PO-04, PO-07). Based solely on dryness ratios and $\delta^{13}C_{CH4}$ values, some of the individual samples from PO-04 and PO-07 had a typical microbial composition, while others seemed to contain thermogenic gas. Therefore, if only one sample per well had been collected, the conclusion could have been that the gas was thermogenic. Because these twin shallow observation wells are located directly on a gas well pad (45 and 50 m from the wellhead, respectively), the simplest explanation for thermogenic gas would have been a leaky gas well. After careful investigation of the processes which can affect methane, the data from these twin wells point towards oxidation of microbial gas; in this case, collecting several samples over time proved key in demonstrating this hypothesis.

*Table 3. Inferred gas origin and biogeochemical processes for all sampled wells containing detectable methane, along with the criteria used to come to these conclusions. An asterisk (*) indicates that methane in a given well has undergone more than one process, and is consequently listed in more than one cell.*

| Gas origin | Process affecting the gas | Criteria indicative of this process | Concerned wells |
|---|---|---|---|
| Microbial | None | • $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$ within the range expected for microbial gas in this region (see sections 6.2.1 and 6.2.2, respectively)<br>• $\delta^{13}C_{DIC}$ within the range expected for this region (see section 6.2.1), and necessarily below 0‰. | RES-04, PO-11 |
| | Late-stage methanogenesis | • $\delta^{13}C_{DIC}$ above 0‰<br>OR<br>• $\delta^{13}C_{DIC}$ below 0‰, but both $\delta^{13}C_{CH4}$ and $\delta^{13}C_{DIC}$ fit within the trend modeled for reservoir depletion of substrate and product (see section 6.2.1, Fig. 6). | PO-12* |
| | Oxidation | • $\delta^{13}C_{CH4}$ higher than expected for microbial gas, but not accompanied by correspondingly higher $\delta^{13}C_{DIC}$ (according to the modeled trend, Fig. 6), which could otherwise indicatelate-stage methanogenesis<br>• Possibly low dryness ratio (in case of anaerobic oxidation preferentially degrading methane), but in some cases this is not observed (see section 6.2.2 for details)<br>• $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$ values following the expected trend modeled for oxidation (see section 6.2.2, particularly Fig. 7), especially if multiple samples from the same well plot at different extents of oxidation within this trend. Multiple samples from each well are extremely useful for this purpose. This criterion is the most decisive of all three. | RES-06, PO-04, PO-07 |
| Microbial and thermogenic | Mixing | • Consistent[1] presence of ethane and/or propane<br>• $\delta^{13}C_{CH4}$ between -90 and -50‰, AND dryness ratio between 10 and 1000 (Fig. 5)<br>• If the two criteria above are satisfied, the $\delta^{2}H_{CH4}$ must still be consistent with a thermogenic origin (Fig. 7) | RES-03, RES-05, PO-12* |
| Originally thermogenic, then microbial | Secondary methanogenesis | Either:<br>• Anaerobic, reducing conditions[2]: in this case, anaerobic biodegradation of (possibly thermogenic) methane may occur preferentially, followed by secondary microbial methanogenesis. In this case the presence of thermogenic gas should not be masked, as $C_{2+}$ hydrocarbons would not be degraded In cases where anaerobic hydrocarbon oxidation is paired with sulfate reduction, propane could be degraded preferentially, but not ethane.<br>Or:<br>• Oxic conditions in a part of the aquifer (where preferential $C_{2+}$ biodegradation can occur), followed by migration into an anoxic environment, for instance wetlands (where secondary methane production can occur). These particular flow conditions, which need to be assessed from a groundwater flow model, could lead to thermogenic gas being "masked" by secondary methanogenesis. | None (although this possibility remains for PO-12 |

[1] Here "consistent" implies that for wells where multiple samples are available, the mean concentration is above detection limit (with non-detects being assigned half the detection limit for computation purposes).

[2] Methanogenesis occurs in absence of oxygen and under redox potential (Eh) typically <-200 mV (Conrad, 2020; Whiticar, 1999). However, wells act as "chimneys" open to the atmosphere, such that the water that is sampled from a well may contain small

amounts of dissolved oxygen and somewhat higher redox potential, while the groundwater in the aquifer in the vicinity of the well could still support methanogenesis.

In the Elgin area, methane seems ubiquitous in shallow groundwater, and was detected in 6 out of 7 sampled wells. The gas origin is also more complex: some wells have exclusively microbial gas (RES-04, RES-06, PO-11), in some cases partially oxidized (RES-06), while other wells have a mixture of thermogenic and microbial gas (RES-03, RES-05, PO-12), and one of them contains a certain proportion of late-stage microbial gas (PO-12). Of note, no hydrocarbon production has occurred yet in Elgin, and the 5 exploration wells found in the area are all located more than 2.3 km from the shallow wells containing thermogenic gas, strongly suggesting that the thermogenic gas in shallow groundwater must be naturally occurring. This thermogenic gas appears to be related to the presence of outcropping or shallow-burial Horton Group bedrock, and to geochemically evolved, Na-Cl type groundwater. The complex geology and methane dynamics in the Elgin area underlines that a more extensive baseline study should be conducted in nearby residential wells before any commercial exploitation begins in this area.

## 7 Conclusions

In this study, the methane and higher alkane distribution in groundwater was investigated in the active McCully unconventional gas field and a prospect domain for condensates in the Elgin area, both located in the province of New Brunswick (eastern Canada), where a moratorium on hydraulic fracturing is currently in place due to environmental and health concerns. Groundwater was sampled both in residential wells and in monitoring wells specifically drilled for this project, many of which were located directly on gas well pads (less than 75 m from the wellhead). In shallow groundwater throughout the whole study area, hydrocarbon concentrations and origin, as well as TDS, were found to be unrelated to proximity to gas wells. Also, none of the regulated metals, anions or VOCs exceeded the health-related guidelines. Hence, based on these results, hydraulic fracturing activities that went on between 2003 and 2015 in the McCully gas field do not appear to have negatively impacted shallow groundwater resources.

In the McCully gas field, methane (and sometimes ethane) were detected in a few samples from wells drilled directly on gas well pads, but the origin of these gases was determined to be microbial after an in-depth investigation of four different processes that can affect their composition. In the Elgin prospective area, where only five exploration wells have been drilled and no commercial production has yet taken place, methane and higher alkanes appear to be ubiquitous in the shallow aquifer. The origin of the gas in this area was found to be more complex, involving thermogenic gas in some cases.

More generally, this field study clearly demonstrates that without a comprehensive approach and the conduct of groundwater monitoring over an extended period (minimally 5-6 samples per well over a period of 2 years), conclusions on the origin of gas in some wells may be erroneous, with potentially undesirable and serious implications for all stakeholders. Here, the conclusions on gas origin were made possible by a systematical multi-isotope approach, which uses site-specific data to assess the occurrence of major processes that may alter the gas composition and isotopic signature, and thus allows identifying the gas origin with greater certainty. This approach relies on three critical aspects, namely: 1) collecting repeat samples in each well over an extended period; 2) analyzing key geochemical and isotopic parameters (concentrations of anions, cations, and $C_1$-$C_3$ hydrocarbons, and $\delta^{13}C_{CH4}$, $\delta^{2}H_{CH4}$, $\delta^{2}H_{H2O}$, $\delta^{13}C_{DIC}$); and 3) using equations and fractionation factors from the literature, along with data from the site, to model site-specific trends for the different biogeochemical processes. The findings that were made possible by this approach are critical and apply to any hydrocarbon-related environmental study, especially where aquifers contain low to moderate dissolved concentrations of methane and ethane, which is very often the case. We therefore recommend that this approach be adopted to determine the origin of hydrocarbons in groundwater, and be implemented by the various jurisdictions to complement their current legislation.

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# Appendices

## Appendix A: Well information and chemical results

<u>**For well information and chemical results, see Excel file**</u>

Notes:

1) For observation wells, both the total well depth and the sampling depth (based on targeted productive fractures) are indicated. For residential wells, only the total well depth was generally known. The sampling depth was assumed to be the same as the total depth, because pumps are normally positioned close to the bottom of the well.

2) For chemical analytical parameters, whenever available, criteria are listed that are either health-based (enforceable), or aesthetics-based (non enforceable). In either case, the regulatory organization responsible for these criteria is indicated. "OCMOH" is the Office of the Chief Medical Officer of Health of New Brunswick (OCMOH, 2020), and "Health Can" is Health Canada (2019).

3) Cells highlighted in green indicate that the aesthetic criterion was exceeded. No exceedance of health-based criteria were observed.

4) For bromodichloromethane, dibromochloromethane, tribromomethand and chloroform, a health-based criterion of 0.1 mg/L is indicated, with an asterisk (*). These compounds are indeed regulated, but the criterion applies to the sum of these trihalomethanes (see column AF for the sum).

5) Results for volatile organic compounds (VOCs) are shown only for the compounds that were detected in at least one sample. The complete list of analyzed VOCs is found below.

| Compound | Detection limit (mg/L) |
|---|---|
| tribromomethane | 0.00014 |
| dichloroethene | 0.00012 |
| DCM | 0.00014 |
| dichloroethene | 0.00014 |
| dichloroethane | 0.00016 |

| | |
|---|---|
| dichloroethene | 0.00023 |
| 2,2 dichloropropane | 0.00023 |
| trichloromethane | 0.00016 |
| bromochloromethane | 0.00012 |
| trichloroethane | 0.00012 |
| tetrachloromethane | 0.00020 |
| 1,2-dichloro-1-propene | 0.00020 |
| benzene | 0.00015 |
| 1,2-dichloroethane | 0.00015 |
| trichloroethylene | 0.00016 |
| 1,2-dichloropropane | 0.00015 |
| dibromomethane | 0.00016 |
| bromodichloromethane | 0.00014 |
| 1,3-dichloropropene | 0.00020 |
| toluene | 0.00009 |
| 1,3-dichloropropene | 0.00020 |
| 1,1,2-trichloroethane | 0.00012 |
| 1,3-dichloropropane | 0.00016 |
| tetrachloroethylene | 0.00008 |
| dibromochloromethane | 0.00016 |
| 1,2-dibromoethane | 0.00027 |
| chlorobenzene | 0.00009 |
| 1,1,1,2-tetrachloroethane | 0.00012 |
| ethylbenzene | 0.00012 |
| m-xylene | 0.00007 |
| o-xylene | 0.00007 |
| styrene | 0.00007 |
| tribromomethane | 0.00020 |
| isopropylbenzene | 0.00007 |
| tetrachloroethane | 0.00016 |
| 1,2,3-trichloropropane | 0.00016 |
| bromobenzene | 0.00010 |
| propylbenzene | 0.00007 |
| 2-chlorotoluene | 0.00009 |
| trimethylbenzene | 0.00006 |
| 4-chlorotoluene | 0.00008 |
| tert-butylbenzene | 0.00008 |
| trimethylbenzene | 0.00007 |
| (1-methylpropyl)benzene | 0.00007 |
| isopropyltoluene | 0.00007 |
| dichlorobenzene | 0.00007 |
| dichlorobenzene | 0.00009 |
| butylbenzene | 0.00010 |
| dichlorobenzene | 0.00009 |
| trichlorobenzene | 0.00081 |
| 1,2-dibromo-3-chloropropane | 0.00020 |
| hexachlorobutadiene | 0.00018 |
| naphthalene | 0.00027 |
| trichlorobenzene | 0.00024 |

## Appendix B: Analytical procedures for alkane isotopic composition at the Geological Survey of Canada

**Analysis:** The 1-L amber glass bottles were placed on their sides and helium was injected through the butyl septa to create a headspace volume between 5 to 60 mL while allowing an equal volume of water to escape. The bottles were manually shaken for several minutes and left to equilibrate for several hours. Between 10 to 1200 µL of gas was extracted from the headspace using an airtight syringe and manually injected into a TRACE 1310 gas chromatograph (GC) equipped with an Agilent J&W GS-Carbonplot column (30 m × 0.32 mm × 3.0 µm) interfaced with a Delta V isotope ratio mass spectrometer (IRMS) via a GC IsoLink system (Thermo Fisher Scientific, Bremen, Germany). The injector temperature was 200°C and the GC was kept at room temperature. For $\delta^{13}C$ analyses, samples pass through a high temperature (1050°C) combustion furnace, where all hydrocarbon gas species are quantitatively converted to $CO_2$. For computing the isotopic composition of samples, an internally calibrated $CO_2$ reference (monitoring) gas with known $\delta^{13}C$ values was used. The $\delta^{13}C$ value of this reference gas was determined using $CO_2$ calibrated against international carbonate standards (NBS 18, NBS 19 and LSVEC). For $\delta^{2}H$ analyses, samples pass through a high temperature (1420°C) pyrolysis furnace, where all hydrocarbon gas species are quantitatively converted to $H_2$. For computing the isotopic composition of samples, a commercial $H_2$ isotopic reference gas was used (Oztech Trading Corporation, Safford, AZ), which was calibrated against the VSMOW international standard. Both reference gases were introduced into the system via bellows. All sample measurements were corrected using calibration curves made from isotopically distinct methane standards (Isometric Instruments, Victoria, BC, Canada): B-iso1 ($\delta^{13}C$ = -54.5‰, $\delta^{2}H$ = -266‰), L-iso1 ($\delta^{13}C$ = -66.5‰, $\delta^{2}H$ = -171‰), and H-iso1 ($\delta^{13}C$ = -23.9‰, $\delta^{2}H$ = -156‰). Precision is ≤ 0.5‰ for $\delta^{13}C$ and ≤ 3.0‰ for $\delta^{2}H$.

**Quality control:** The linearity range is defined at the beginning of each day, using the reference (monitoring) $CO_2$ and $H_2$ gases, in order to ensure that peak heights for all reported samples (even those with low methane concentrations) are within the linearity range. Then, for every analysis, a peak of the reference gas is sent before the sample (the known isotopic composition of this reference gas being imposed and serving to compute the isotopic composition of the upcoming sample), and two peaks of the reference gas are sent again after the sample, for quality control. In order to correct the measured sample isotopic composition (in case a small fractionation occurs as samples are passed through the system), the international methane standards (B-iso1, L-iso1, H-iso1) are injected at the beginning of each day, to build a two point calibration curve; the accuracy of the curve is checked with the third standard, having the mid-range isotopic value. These standards are injected again at the middle and at the end of the day, to verify that instrument drift did not compromise results. Furthermore, every sample was injected a minimum of two times for $\delta^{13}C$, and three times for $\delta^{2}H$, to ensure that the results from multiple injections lie within the targeted method precision.

## Highlights

- Methane and higher alkanes are found in groundwater near Sussex, New Brunswick
- A multi-isotope approach is used to infer the origin of these hydrocarbons
- Four biogeochemical processes that commonly blur interpretation are scrutinized
- Microbial gas is largely predominant, but thermogenic gas occurs in some wells
- Microbial gas in many wells exhibits late-stage methanogenesis, oxidation or mixing

**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

The authors have no competing interest to declare. Staff and management at Corridor Resources have greatly collaborated to this project by providing access to their sites (well pads, gas plant) for us to install scientific equipment (wells, precipitation collector). As they were on-site year-round, they also graciously collected monthly precipitation from our apparatus (for later isotopic analyses) over one year. They did not participate in result interpretation, or paper writing or reviewing.