

# Comparison of isotopic compositions of hydrocarbon gas in shallow groundwater and a deep oil and natural gas reservoir in southeastern New Brunswick, Canada

DIANA B. LOOMER<sup>1\*</sup>, KERRY T.B. MACQUARRIE<sup>1</sup>, TOM A. AL<sup>2</sup>

1. Department of Civil Engineering, University of New Brunswick,  
Fredericton, New Brunswick E3B 5A3, Canada

2. Department of Earth and Environmental Science,  
University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

\*Corresponding author <dloomer@unb.ca>

*Date received: 17 January 2020* † *Date accepted: 30 July 2020*

## ABSTRACT

Isotopic analyses of natural gas from the Stoney Creek oil field in New Brunswick indicate carbon ( $\delta^{13}\text{C}$ ) and hydrogen ( $\delta^2\text{H}$ ) values in methane ( $\text{C}_1$ ) of  $-42.4 \pm 0.7\text{‰}$  VPDB and  $-220.9 \pm 3.2\text{‰}$  VSMOW, respectively. Isotopic data and a gas molecular ratio of  $12 \pm 1$  indicate a wet thermogenic gas formed with oil near the onset of the oil-gas transition zone. The isotopic profiles of the  $\text{C}_1$ – $\text{C}_5$  hydrocarbon gases are consistent with kinetic isotope effect models. The Albert Formation of the Horton Group hosts the Stoney Creek oil field (SCOF) and the McCully gas field (MCGF) the only other gas-producing field in the province. Both are thermogenic in origin; however, the SCOF gas has a lower thermal maturity than the MCGF. Hydrocarbon gas composition in shallow aquifers across southeastern New Brunswick was also evaluated. Gas source interpretations based on  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  values are uncertain; oxidation and biogenic overprinting are common and complicate interpretation. The effect of oxidation on  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  values was apparent when  $\text{C}_1$  concentrations were  $\leq 1$  mg/L. In some samples with  $\text{C}_1$  concentrations  $> 5$  mg/L, isotopic discrimination methods point to a biogenic origin. However, the molecular ratios  $< 75$  and the presence of  $> \text{C}_3$  fractions, indicate a thermogenic origin. This suggests a thermogenic isotopic signature has been overprinted by biological activity.

---

## RÉSUMÉ

Les analyses isotopiques du gaz naturel en provenance du champ pétrolifère de Stoney Creek au Nouveau-Brunswick révèlent des concentrations de carbone ( $\delta^{13}\text{C}$ ) et d'hydrogène ( $\delta^2\text{H}$ ) dans le méthane ( $\text{C}_1$ ) de  $-42,4 \pm 0,7 \text{‰}$  de VPDB (bélemnites de Pee Dee de Vienne) et de  $-220,9 \pm 3,2 \text{‰}$  de VSMOW (eau océanique moyenne normalisée de Vienne), respectivement. Les données isotopiques et un coefficient moléculaire du gaz naturel de  $12 \pm 1$  signalent qu'un gaz thermogénique humide s'est formé en association avec du pétrole près du commencement de la zone de transition entre le pétrole et le gaz naturel. Les profils isotopiques des gaz d'hydrocarbures  $\text{C}_1$ – $\text{C}_5$  correspondent aux modèles de l'effet isotopique cinétique. La Formation d'Albert du groupe de Horton abrite le champ pétrolifère de Stoney Creek (CPSC) et le champ pétrolifère McCully (CPMC), seul autre champ producteur de gaz naturel dans la province. Les deux sont d'origine thermogénique, mais le gaz du CPSC a une maturité thermique inférieure au CPMC. La composition en gaz d'hydrocarbures des formations aquifères peu profondes

dans le sud-est du Nouveau-Brunswick a elle aussi été évaluée. Les interprétations des sources de gaz naturel basées sur les concentrations de  $\delta^{13}\text{C}$  et de  $\delta^2\text{H}$  sont incertaines. L'oxydation et la surimpression biogénique sont courantes et compliquent l'interprétation. L'effet de l'oxydation sur les concentrations de  $\delta^{13}\text{C}$  et de  $\delta^2\text{H}$  était visible lorsque les concentrations de  $\text{C}_1$  étaient  $\leq 1$  mg/L. Dans un certain échantillon comportant des concentrations de  $\text{C}_1$  de  $>5$  mg/L, les méthodes de discrimination isotopique indiquent une origine biogénique. Les coefficients moléculaires de  $<75$  et la présence de fractions de  $>\text{C}_3$  révèlent toutefois une origine thermogénique. Cela laisse supposer qu'une signature isotopique thermogénique s'est superposée dans le cadre d'une activité biologique.

[Traduit par la rédaction]

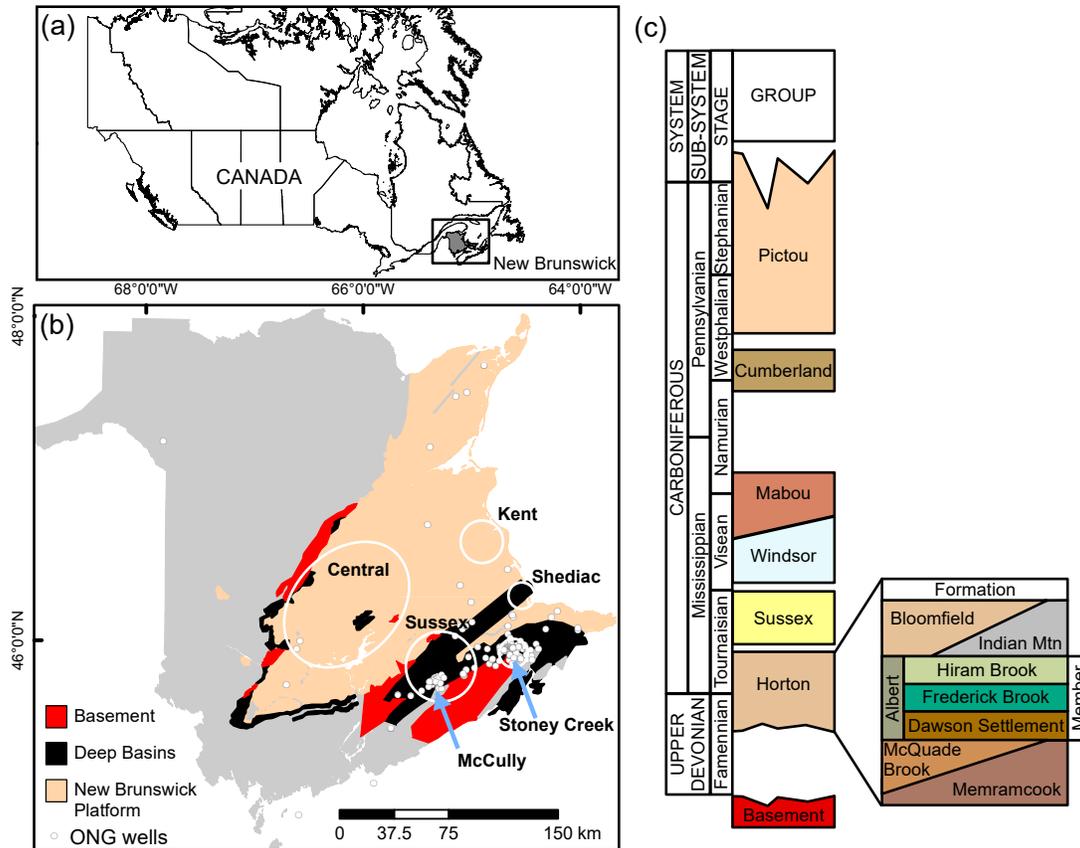
## INTRODUCTION

Commercial hydrocarbon production in New Brunswick extends back to the mid-Nineteenth Century, when the province exported bitumen mined from oil-shale and albertite (solid bitumen) deposits at Albert Mines, located approximately 25 km southeast of Moncton (Martin 2003). Early hydrocarbon exploration focused on known oil and gas seepages in the area south of Moncton (Foley 1989), and one of the first oil wells in North America was drilled in 1859 at Dover, east of the Peticodiac River (St. Peter 2000). Oil-bearing rock in the first production well was encountered at an approximate depth of 27 m (Martin 2003), indicating near surface occurrences of hydrocarbon-bearing units. Until recently, however, the most significant oil and natural gas (ONG) production has come from the Stoney Creek field (St. Peter 2000). It is located west of the Peticodiac River, approximately 20 km south of Moncton (Fig. 1). In that area of the field, well depths range from approximately 800 to 1500 m. The field began producing primarily gas in 1910, with a peak annual production of  $2.4 \times 10^7 \text{ m}^3$  (860 mmscf). In the mid-1920s, oil production increased, peaking at  $4500 \text{ m}^3$  (30 000 bbls) per annum. In the late-1940s, the field saw a rapid drop in gas production, while oil production declined more slowly until production stopped in 1991. Oil production recommenced in 2007 and continues today, with a maximum annual production since then of  $5000 \text{ m}^3$ . The Stoney Creek oil field (SCOF) currently includes approximately 160 wells: three are horizontal wells and the rest are vertical wells. Provincial records indicate that most wells have been abandoned, but approximately 34 are either shut in or producing. Another  $\sim 50$  nonproducing wells are located outside the main SCOF area. In 2000, 55 km to the southwest of the SCOF, gas was discovered at a depth of approximately 2500 m. The field is identified as the McCully gas field (MCGF). Production at the MCGF began in 2003 and had peak gas production of  $2.1 \times 10^{16} \text{ m}^3$  in 2008. Provincial records indicate that there have been 39 ONG wells drilled in the field. The wells are vertical or inclined and were hydraulically fractured (Jiang *et al.* 2016).

Hydrocarbon resources from the two ONG fields, and from Albert Mines, are associated with the lacustrine hydrocarbon-bearing shales and sandstones of the Albert Formation. Conventional and fracture-stimulation

extraction techniques have been used in the SCOF throughout its history (St. Peter 2000), whereas the MCGF has required fracture stimulation to achieve commercial production rates (Corridor Resources Inc. 2019). With recent advances in horizontal well drilling and hydraulic fracturing (i.e., unconventional ONG extraction), the natural gas and oil held in the Albert Formation shales and tight sandstones may be extracted at economical rates in other areas of the province. However, the surge in unconventional ONG extraction has brought intense scrutiny to the petroleum industry from the public, governments and academics (Vidic *et al.* 2013).

Oil and natural gas production generates concerns regarding the risk to freshwater resources from contamination resulting from wellbore integrity failure, wastewater discharge and accidental spills at the surface (Vengosh *et al.* 2014). This has prompted a wide range of research, including many regional groundwater studies attempting to determine impacts from pre-existing unconventional ONG production (McMahon *et al.* 2017) and in areas of potential unconventional development (Harkness *et al.* 2018; McIntosh *et al.* 2014; Moritz *et al.* 2015). Other evaluations have been conducted before, during and after unconventional ONG extraction (Harkness *et al.* 2017). Studies of this type commonly focus on shallow potable water aquifers in the region of interest and include the collection of data on the molecular composition of the gas, methane ( $\text{C}_1$ ), ethane ( $\text{C}_2$ ) and propane ( $\text{C}_3$ ) content, and the isotopic compositions of carbon ( $\delta^{13}\text{C}$ ) and hydrogen ( $\delta^2\text{H}$ ) in  $\text{C}_1$ . The isotopic composition of hydrocarbon gases can indicate if the gases were formed through microbial action, commonly referred to as biogenic gas, or through abiotic cracking of oil or kerogen, commonly referred to as thermogenic gas (Schoell 1983; Whiticar 1999; Milkov and Etiope 2018). The isotopic compositions of hydrocarbon gases may also be used as tracers to identify natural connections to hydrocarbon reservoirs or pathways for stray gas entering shallow aquifers due to ONG resource developments (Sharma *et al.* 2014). However, to be useful as a tracer, the isotopic composition of the gas source must be known. Barton (2018) characterized gases from the MCGF, but isotopic characterization of gas from the SCOF has not been carried out. Therefore, the first objective of the work presented here was to determine the isotopic composition of hydrocarbon gases from the SCOF.



**Figure 1.** (a) Map of Canada with the province of New Brunswick shown in grey. (b) The Maritimes Basin in New Brunswick (after St. Peter and Johnson 2009). The locations of the study areas, producing and abandoned oil and natural gas (ONG) wells and the Stoney Creek and McCully ONG fields are indicated. (c) Stratigraphic column of the Maritimes Basin in New Brunswick after Hinds and St. Peter (2006) and Park (2014).

In 2014, the New Brunswick Energy Institute commissioned a regional baseline groundwater study across southeastern New Brunswick (Loomer *et al.* 2016). The first objective of the study was to collect and report on private well-water chemistry in regions that the petroleum industry had identified as potential targets for unconventional ONG exploration and development. In 2017, additional regional well-water sampling in the vicinity of the SCOF was carried out (Loomer and MacQuarrie 2018). The groundwater chemistry data compiled in these two studies included dissolved hydrocarbon gas content and their isotopic compositions. The second objective of the present work was to evaluate the isotopic composition of hydrocarbon gases detected in shallow groundwater, including the rarely reported isotopic composition of  $C_2$ , and compare them to the chemical and isotopic compositions of gases from the ONG fields. Similarities in the molecular and isotopic compositions of the hydrocarbon gases at depth and in shallow groundwater can be an indication of direct and rapid transport of the gases toward the surface, possibly facilitated

by conduits such as natural open fractures or leaking well bores. However, the isotopic compositions of hydrocarbon gases may be altered as a result of secondary effects such as migration, mixing and microbial action (Whiticar 1994). Using the data from the two regional groundwater studies, data from the MCGF (Barton 2018), and additional hydrocarbon data from the SCOF, this work seeks to identify the presence of such effects and to use additional hydrocarbon data, along with knowledge of the local geology, to aid in the assessment of the gas origins in shallow groundwater. In doing so, it incorporates a more complete, updated and detailed interpretation of the groundwater data from Loomer *et al.* (2016) and Loomer and MacQuarrie (2018).

## STUDY SETTING

The study is set within the late Paleozoic Maritimes Basin of Atlantic Canada (Fig. 1), a successor basin that formed subsequent to the Early to Middle Devonian Acadian

Orogeny. It developed in five cycles of subsidence and deposition punctuated by basin inversion/uplift and erosion throughout the Carboniferous Period (Wilson and White 2006). It is characterized by thick deposits of predominantly sedimentary rocks that were formed in alluvial, fluvial, lacustrine and marine environments. St. Peter and Johnson (2009) provided a compilation of previous work on the stratigraphic and structural evolution of the Maritimes Basin in New Brunswick. Briefly, the basin is divided into six main stratigraphic units. In order of decreasing age, they are the Horton, Sussex, Windsor, Mabou, Cumberland, and Pictou groups. The Horton Group is composed of alluvial and freshwater lacustrine strata and overlies a pre-Late Devonian crystalline basement complex. The Sussex Group, a sequence of continental clastic rocks deposited during a more arid interval, truncates the Horton Group with an angular unconformity. The Windsor Group formed as a result of a marine incursion and unconformably overlies the Sussex Group. It comprises coarse-grained clastic rocks and red mudstones, together with carbonates, gypsum, anhydrite, halite and local potash beds. The coarse-grained clastic red beds of the Mabou Group overlie the Windsor strata. The Cumberland Group unconformably overlies the Mabou Group and consists primarily of terrestrial red and grey conglomerates and coarse sandstones with lesser mudstones and minor coal seams. The youngest group in the sequence, the Late Pennsylvanian Pictou Group, is made up of fining-upward fluvial cycles of grey and red sandstones and mudstones with coal seams. The Maritimes Basin includes a series of deep, northeast-trending grabens, commonly referred to as subbasins, separated by intervening horsts. The New Brunswick Platform is a horst and the subbasins are infilled with Horton, Sussex, Windsor and Mabou group rocks. The Cumberland and Pictou groups form a cover sequence that unconformably overlies strata in the older subbasins, with the Pictou Group covering most of the New Brunswick Platform.

The units most relevant to commercial ONG production in the province are the Dawson Settlement, Frederick Brook and Hiram Brook members of the Albert Formation in the Horton Group (Fig. 1c). The present-day maximum burial depth is approximately 5 km in the Sussex area (Park 2014). Keighley (2008) described the members of the Albert Formation in terms of a tectonically controlled, wedge-shaped lacustrine basin, where the Dawson Settlement and Frederick Brook members represent the sediment-starved, lacustrine-dominated stage. The basin then infilled with the predominantly deltaic and fluvial-floodplain sediments of the Hiram Brook Member. The three members are considered to be gradational with lateral interfingerings of lithologies (sandstones and shales) (St. Peter and Johnson 2009). The primary zone of gas production from the SCOF was the Hiram Brook Member, and the primary oil producing zone involved sandstones of the Dawson Settlement Member

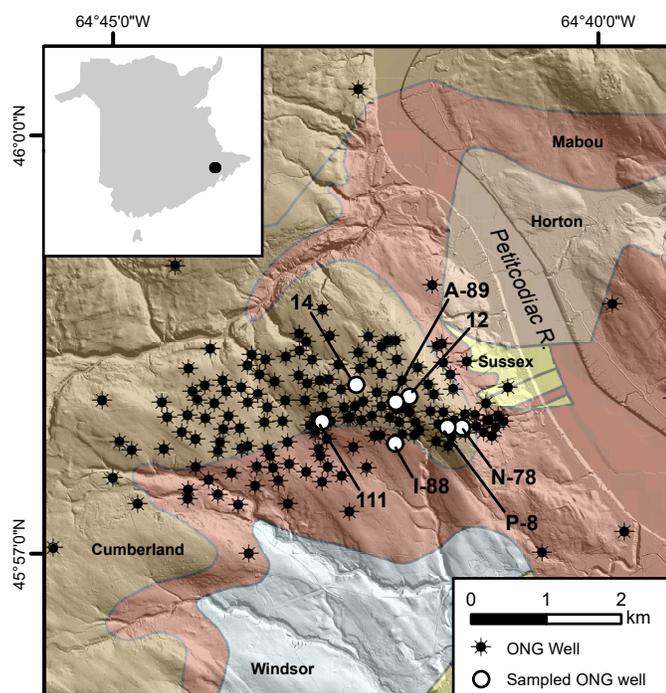
(Foley 1989; St. Peter and Johnson 2009). However, oil-rich zones in the Hiram Brook Member at the SCOF are also known (Chowdhury *et al.* 1991). In the MCGF, the targets for gas have been the Hiram Brook and Frederick Brook members (Park 2014; Barton 2018).

The present study is focused on the five areas within the Maritimes Basin that were included in two recent regional groundwater studies (Fig. 1b; Loomer *et al.* 2016; Loomer and MacQuarrie 2018). Three of these — the Central, Kent and Shediac areas — had been targeted for ONG exploration but have yet to see resource development activities. The other two areas have seen limited (Sussex) to extensive (Stoney Creek) ONG development. The Sussex area includes the MCGF, and the Stoney Creek area extends over a 10-km radius from the centre of the SCOF. The Central and Kent areas are located on the New Brunswick Platform; the majority of the groundwater wells in these two study areas are completed in the Pictou Group. The Shediac area straddles the Cocagne subbasin, the Indian Mountain deformed zone, and the Westmorland uplift (St. Peter and Johnson 2009); however, the surficial bedrock primarily belongs to the Pictou Group. The Sussex and Stoney Creek areas are located within the Moncton subbasin, with faulted and folded strata from all geologic groups of the Maritimes Basin outcropping at surface.

## SAMPLING AND ANALYSES

The SCOF produces mainly oil; however, natural gas is captured from the wellheads and used to power machinery on site. On 29 October 2018, samples of this gas were collected at the wellhead from seven producing wells (Fig. 2). The sampled wells include three horizontal boreholes drilled in 2006 and 2008 that targeted the Dawson Settlement Member (wells A-89, I-88 and N-78). Four previously shut-in wells (12, 14, 111 and P8), which date from as early as 1910, were re-entered in 2007, and these were also sampled. Well depths range from 800–1580 m, and current oil production is from the Dawson Settlement Member (Acadian Securities 2007; Orlen 2019). The older wells were originally open holes below the Hiram Brook Member (St. Peter and Johnson 2009), and natural gas production was primarily from the Hiram Brook Member, whereas the main oil producing unit was the Dawson Settlement Member (Foley 1989). Casing and perforation details from the horizontal and recompleted wells were not disclosed, but extraction from multiple units is possible (Acadian Securities 2007). Therefore, the production of natural gas cannot be constrained to a specific unit. Gas samples were collected in Isotubes® (IsoTech Laboratories, Champaign IL, USA) using a pressure-controlling sampling manifold.

Groundwater data are reported for a subset of 52 wells from the two regional studies (Loomer and MacQuarrie 2018;



**Figure 2.** Location of sampled oil and natural gas (ONG) wells within the Stoney Creek oil field (SCOF) overlain on bedrock geology (NBDNR 2008 and St. Peter and Johnson, 2009) and lidar-based topography (NBDERD 2019). Sedimentary groups of the Maritimes Basin and the Peticodiac River are indicated. Producing, shut-in and abandoned ONG wells shown.

Loomer *et al.* 2019). The dataset represents groundwater with dissolved  $C_1$  concentrations  $>0.1$  mg/L and includes wells located within all five study areas. All wells sampled in the Central, Kent, Shediac and Sussex areas are located more than 800 m from an ONG well. In the Stoney Creek area, the horizontal distance between the water wells and the nearest ONG well ranges from 85–4900 m. The water wells were sampled twice, the second including the collection of samples for the determination of  $\delta^{13}C$  and  $\delta^2H$  in  $C_1$ . The isotopic composition of  $C_2$  was also determined from Stoney Creek well water samples when  $C_2$  concentrations were  $>0.1$  mg/L. Samples were collected between June and October in 2014, 2015 and 2017. The time between the collection of the first and second samples for each well ranged from 13 to 349 days, but was typically on the order of 40 days.

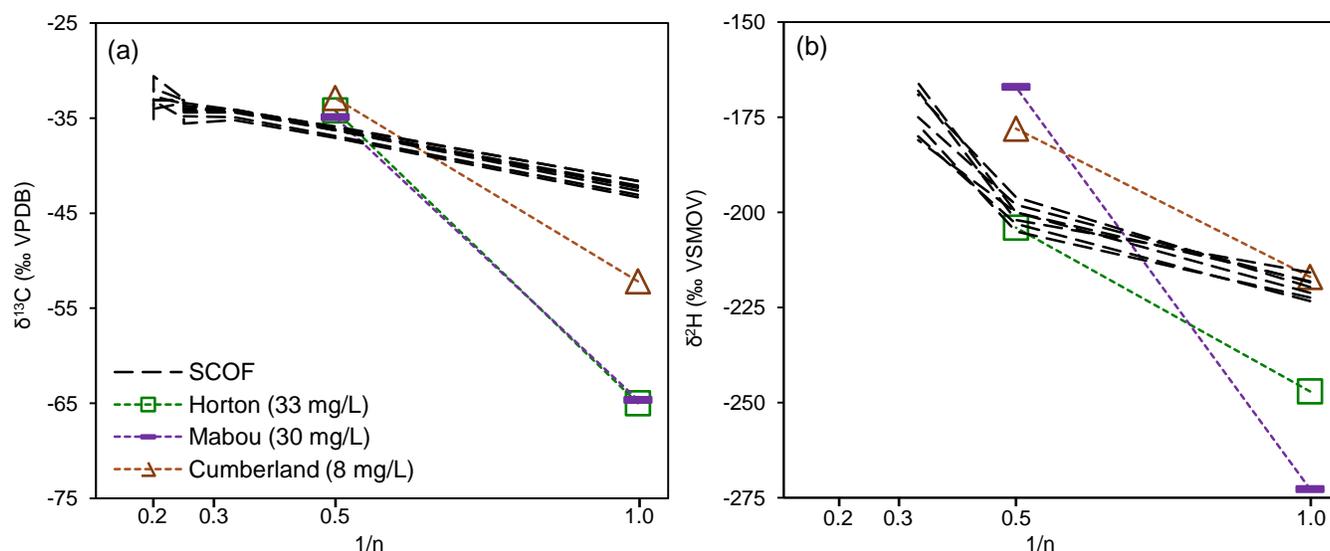
All water wells had standard 15-cm-diameter steel casing through overburden and were completed as open holes in bedrock, or with slotted well screens when completed in unconsolidated sediments or erodible shale. Well depths ranged from 6 to 88 m, with a median depth of 37 m. The wells supplied water to private homes, businesses or farm buildings and had pressure tanks to maintain relatively

constant pressure. All samples were collected upstream of any water treatment systems present. Sampling and analysis followed the procedures described in Loomer *et al.* (2016, 2018) and Loomer and MacQuarrie (2018). Samples were collected upon stabilization of the field parameters (pH, specific conductance, dissolved oxygen and  $E_h$ ). Samples for dissolved hydrocarbon gases were collected using the submersed vial method. Analyses for the molecular composition of the hydrocarbon gases were conducted at the Research and Productivity Council in Fredericton, New Brunswick, using a Bruker Gas Chromatograph coupled to a Flame Ionization Detector (method AQS90). The results from the headspace analyses were converted to aqueous concentrations using Henry's Law. The instrument detection limit was 0.0001 mg/L and the detection limit based on field blanks was 0.0005 mg/L for  $C_1$  and 0.0001 mg/L for  $C_2$  and  $C_3$ . Results from field blank and replicate samples are provided in Tables A1 and A2 in Appendix A. The presence/absence of ethene ( $C_{2=}$ ), propene ( $C_{3=}$ ), butane, pentane and hexane ( $C_4$ – $C_6$  hydrocarbons) were also evaluated in groundwater samples from the Stoney Creek area. Standards were injected into the instrument to obtain the retention time for each compound and the GC software CompassCDS™ (Scion Instruments, Edmonton, Alberta) was used to identify peaks in the two sample chromatographs (Appendix B). Quantification of  $C_{2=}$ ,  $C_{3=}$ , and  $C_4$ – $C_6$  was not available.

Molofsky *et al.* (2016) found that there was a significant difference in dissolved  $C_1$  concentrations between open direct-fill, semi-closed (similar to this study) and closed (IsoFlask®) techniques when  $C_1$  concentrations were  $>20$  mg/L. To evaluate possible losses from the sampling set-up used in this work, 42 wells in the Stoney Creek area were sampled using both the submersed-vial and IsoFlask® methods (Loomer and MacQuarrie 2018). Methane concentrations determined using the IsoFlask® method were up to 15 mg/L higher than those determined from the submersed-vial method when  $C_1$  concentrations were  $>15$  mg/L. Based on the data from Loomer and MacQuarrie (2018), the following relationship was used to correct concentrations from the submersed vial technique (vial, mg/L) to equivalent IsoFlask® concentrations (Corrected, mg/L) for samples that were not collected with IsoFlasks:

$$\text{Corrected} = 0.0394[\text{vial}]^2 + 0.854[\text{vial}] + 0.0539 \quad (R^2 = 0.9984) \quad \text{Eq. 1}$$

Samples for dissolved gas isotopic analysis were collected in the same manner as for dissolved gas concentrations, either in IsoFlasks® or in submersed 700-mL glass Wheaton bottles with screw caps and butyl rubber septa, preserved with 6N HCl. Isotopic and compositional analyses for Stoney Creek produced gas and the isotopic analyses of dissolved gases in groundwater were conducted at the Ján



**Figure 3.** (a) Chung plot of  $\delta^{13}C_1$  versus reciprocal carbon number ( $n$ ) for SCOF and groundwater samples from the Stoney Creek area with ethane concentrations  $> 0.1$  mg/L. Groundwater samples identified by bedrock geology with dissolved methane concentration provided in brackets. (b) Corresponding cross plot of  $\delta^2H$  versus reciprocal carbon number.

Veizer Stable Isotope Laboratory at the University of Ottawa. The chemical composition of the gas samples ( $O_2$ ,  $CO_2$ ,  $N_2$  and hydrocarbons  $C_1$ – $C_5$ ) was measured using an SRI 8610C dual column gas chromatograph fitted with flame ionization and thermal conductivity detectors. Methane and ethane were extracted from the groundwater samples using the headspace equilibrium technique. Stable carbon and hydrogen isotope measurements of the hydrocarbon gases,  $C_1$  to  $C_3$  were conducted if concentrations were above 0.08% in the gas phase. The isotopic compositions of  $C_4$  and  $C_5$  were reported when their peaks in the GC could be resolved. Analyses were performed using a Thermo-Fisher Delta V Isotope Ratio Mass Spectrometer interfaced via a Conflow 4 to an Agilent 8790A gas chromatograph equipped with a combustion furnace (1000°C) for carbon oxidation to  $CO_2$ , and a pyrolysis furnace (1420°C) for hydrogen conversion to  $H_2$ . The National Institute of Standards certified reference standards NGS1 and NGS2 were used for the  $^{13}C$  and  $^2H$  in  $C_1$  calibration for groundwater samples from the Central, Kent, Shediac and Sussex study areas. For the analyses of the groundwater samples from the Stoney Creek area and the Stoney Creek production gas samples, the USGS HCG-1, -2 and -3 standards were used. The USGS standards offer standardized values for  $^{13}C$  and  $^2H$  in  $C_1$ – $C_3$ . No certified standards were available for  $C_4$  and  $C_5$ . Therefore, peak retention times were confirmed with a  $C_1$ – $C_6$  gas composition standard (Air Liquide, Ottawa), and the isotopic calibration for  $C_3$  was applied to  $C_4$  and  $C_5$ . Carbon dioxide concentrations in the gas samples were too low for reliable isotopic measurements.

Differences in  $\delta^{13}C$  values for field duplicate gas samples

ranged from 0.0–0.7‰, showing no apparent trends with carbon number or isomer. Therefore, the reported  $\delta^{13}C$  uncertainty is based on the maximum difference measured,  $\pm 0.7$ ‰, for all hydrocarbon gases. Differences in  $\delta^2H$  for duplicate samples ranged from 0.3–2.0‰, with uncertainty increasing from  $C_1$  to  $C_3$ . Hold times for the dissolved gas samples varied from 1–9 weeks due to capacity limitations of the analytical laboratory. Evaluation of the effects of prolonged hold times showed no correlation between  $\delta^2H$ – $C_1$  values and sample hold times; however, the  $\delta^{13}C_1$  values became progressively depleted over time (Loomer *et al.* 2018). Therefore, the maximum estimated uncertainty in  $\delta^{13}C_1$  based on the regression analysis presented in Loomer *et al.* (2018) and the hold times for samples in this study is  $-4.6$ ‰. The uncertainty in  $\delta^2H$ – $C_1$ , based on duplicate analyses, is  $\pm 4.4$ ‰.

## RESULTS AND DISCUSSION

### Production gas composition

The SCOF gas has a narrow range of compositions and is predominantly  $C_1$  (75–83%) with minor amounts of  $C_2$  (~4%),  $C_3$  (2–3%),  $C_4$  and nitrogen ( $\leq 2\%$  each), and  $C_5$  ( $< 1\%$ ) (Table 1). Gas from the SCOF has a smaller range of molecular ratios,  $C_1/(C_2+C_3)$ , from 10 to 14, than gas from the MCGF, which ranges from 9 to 59 (Barton 2018). The concentrations of  $n$ - $C_4$  and  $n$ - $C_5$  are greater than those of their respective branched isomers. Only trace amounts of carbon dioxide ( $\leq 0.05\%$ ) were detected. There are no trends

**Table 1.** Composition of gases from the Stoney Creek oil field.

Well ID	Well Depth m	O <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	i-C <sub>4</sub>	n-C <sub>4</sub>	i-C <sub>5</sub>	n-C <sub>5</sub>	H <sub>2</sub> O <sup>2</sup>
							% vol					
N-78	1115	0.081	0.040	0.71	77.56	4.68	2.40	0.56	1.32	0.21	0.37	12.99
14A <sup>1</sup>	797	0.070	0.021	0.68	79.76	4.62	1.96	0.34	0.82	0.10	0.18	11.98
14B <sup>1</sup>	797	0.056	0.020	0.64	79.47	4.56	1.92	0.33	0.81	0.11	0.19	12.41
111	880	0.369	0.008	1.64	74.64	4.74	2.88	0.87	2.08	0.50	0.93	12.21
A-89	1582	0.086	0.017	0.83	78.88	4.83	2.06	0.29	0.73	0.11	0.20	12.46
12	1255	0.202	0.005	1.60	82.73	4.31	1.95	0.26	0.70	0.08	0.16	8.43
P-8A <sup>1</sup>	872	0.064	0.004	0.87	83.10	4.19	1.91	0.35	0.93	0.14	0.26	8.44
P-8B <sup>1</sup>	872	0.215	0.005	1.34	82.56	4.06	1.90	0.35	0.94	0.13	0.25	8.86
I-88	1562	0.069	0.002	0.96	78.83	4.22	2.14	0.48	1.20	0.93	0.41	11.24

<sup>1</sup> Field duplicate samples

<sup>2</sup> Water vapour content estimated as the difference between the sum of the other gases and 100%.

in molecular or isotopic composition versus depth in the range sampled. The average  $\delta^{13}\text{C}-\text{C}_1$  and  $\delta^2\text{H}-\text{C}_1$  values of gas from the SCOF,  $-42\text{‰}$  and  $-221\text{‰}$ , respectively, are less enriched in  $^{13}\text{C}$  and  $^2\text{H}$  than those for gas from the MCGF,  $-36\text{‰}$  and  $-168\text{‰}$ , respectively (Barton 2018). The SCOF samples are indicative of a mature thermogenic gas formed with oil, whereas those of the MCGF are indicative of a post-mature wet gas (Ni *et al.* 2011; Milkov and Etiope 2018).

All Stoney Creek gas samples display a straight-line isotopic profile from C<sub>1</sub> to C<sub>3</sub> ( $R^2 = 1.000$ ), where  $\delta^{13}\text{C}_1 < \delta^{13}\text{C}_2 < \delta^{13}\text{C}_3$  (Fig. 3a). This trend is consistent with that predicted by kinetic isotope effect (KIE) models (Chung *et al.* 1988; Berner *et al.* 1995). While there is little expectation that butanes and pentanes had the same precursor functional group or formation mechanism (Chung *et al.* 1988), 61% of the higher weight hydrocarbons also fall, within error, along the C<sub>1</sub>-C<sub>3</sub> straight lines. The progressive increase of  $\delta^{13}\text{C}$  values from C<sub>1</sub> to C<sub>3</sub> represents a “normal” isotopic profile for the Dawson Settlement member in the SCOF. McCully gas samples from the Hiram Brook member also show a normal isotopic profile, but those of the Frederick Brook member display a partial or full isotopic reversal,  $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2 \leq \delta^{13}\text{C}_3$  (Barton 2018). Isotopic reversal is thought to occur in closed-system, or near-closed-system source rock. As a level of advanced maturity is reached, and with little exchange with adjacent formations, the longer chain hydrocarbons become unstable and decompose to produce  $^{13}\text{C}$ -enriched C<sub>1</sub> in the source rock (Tilley and Muehlenbachs 2013).

In contrast to the  $\delta^{13}\text{C}$  profile,  $\delta^2\text{H}$  values in the SCOF gas (Table 2), although not displaying isotopic reversal, do not exhibit a straight-line profile from C<sub>1</sub> to C<sub>3</sub> (Fig. 3b). Hydrogen isotope data for hydrocarbon gases of higher

weight than C<sub>1</sub>, e.g., C<sub>2</sub> up to C<sub>5</sub>, have not been reported as commonly as  $\delta^{13}\text{C}$  because of analytical limitations and the difficulties for interpretation posed by the possibility for hydrogen isotope exchange with external sources (Schimmelmann *et al.* 2006). In cases where  $\delta^2\text{H}$  data are reported with  $\delta^{13}\text{C}$  values, the isotopic profiles for  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  have been internally consistent, i.e. the two profiles show similar trends (Burruss and Laughrey 2010; Wang *et al.* 2015; Barton 2018). It is not clear why the SCOF samples show different trends in the isotopic profiles for  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$ . However, the non-linear  $\delta^2\text{H}$  profile is consistent with the quantum-chemistry-based cumulative KIE model of Ni *et al.* (2011). Ni *et al.* (2011) show that for  $\delta^2\text{H}-\text{C}_2$  values near those of the SCOF, i.e.,  $-200\text{‰}$ , the KIE model profile is non-linear, but not reversed. The quantum KIE model straightens with both increasing and decreasing thermal maturity. Therefore, both the straight  $\delta^{13}\text{C}$  and kinked  $\delta^2\text{H}$  profiles of the SCOF gases are consistent with KIE models.

Overall, the SCOF gas is distinct from the gas produced from the MCGF, and the tight clustering suggests a common source for the SCOF samples despite the range in well depths and the possibility of contributions from multiple production zones. The lower maturity of the SCOF gas suggests that the Horton Group in the northeastern part of the Moncton subbasin did not reach the burial depths experienced at the MCGF, estimated by Park (2014) to be 5 km and 125 to 150 °C, respectively, assuming a geothermal gradient of 2.5 to 3°C/100 m. This is consistent with previous interpretations of increasing thermal maturity of the Moncton subbasin from the northeast to the southwest (Chowdhury 1991). The presence of significant quantities of both oil and gas in the SCOF, combined with the isotopic

**Table 2.** Hydrogen and carbon isotopic composition of hydrocarbon gases from the Stoney Creek oil field.

Well ID	$\delta^2\text{H}$ (‰) <sup>1</sup>			$\delta^{13}\text{C}$ (‰) <sup>1</sup>						
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	i-C <sub>4</sub>	n-C <sub>4</sub>	i-C <sub>5</sub>	n-C <sub>5</sub>
N-78	-215.8	-202.0	-168.0	-41.7	-35.9	-34.2	-34.1	-33.0	-30.6	-33.2
14A <sup>2</sup>	-221.2	-200.0	-166.0	-42.3	-36.4	-34.2	-33.1	-33.0	-33.1	-
14B <sup>2</sup>	-221.6	-201.0	-164.0	-42.1	-36.2	-34.1	-33.7	-33.2	-33.1	-
111	-222.4	-205.0	-177.0	-43.4	-37.1	-35.2	-35.6	-35.0	-33.2	-35.1
A-89	-223.3	-203.0	-180.0	-42.7	-36.3	-34.4	-34.4	-33.5	-32.7	-33.7
12	-225.3	-202.0	-174.0	-43.1	-36.9	-34.9	-34.8	-	-	-
P-8A <sup>2</sup>	-218.1	-200.0	-181.0	-42.0	-36.2	-34.3	-33.9	-33.7	-33.7	-
P-8B <sup>2</sup>	-218.4	-198.0	-175.0	-41.3	-35.8	-33.9	-34.0	-33.1	-34.4	-
I-88	-219.7	-196.0	-169.0	-42.3	-36.2	-34.3	-34.2	-33.1	-31.9	-32.2

<sup>1</sup>  $\delta^2\text{H}$  is measured relative to VSMOW and  $\delta^{13}\text{C}$  is measured relative to VPDB.

<sup>2</sup> Quality control duplicates

"-" Below detection limit

data, places the SCOF in the later stages of the oil window, at temperatures of ~90–120°C and a burial depth of 3–4 km (assuming a geothermal gradient of 3°C/100 m).

The molecular and isotopic compositions of gas from the SCOF and MCGF are used as reference points in the following evaluation of hydrocarbons in shallow groundwater. Similarities between the hydrocarbons associated with the deep ONG fields and hydrocarbons detected in shallow groundwater can be an indication of connections between the deep hydrocarbon reservoirs and the shallow aquifers (Sharma *et al.* 2014). Such connections could include leaking ONG wells and naturally transmissive faults.

### Hydrocarbon gases in shallow groundwater

Dissolved C<sub>1</sub> concentrations in the shallow groundwater ranged from 0.06 to 58 mg/L (Table 3). The IsoFlask® correction increases the highest value measured with the submersed vial method from 29 to 58 mg/L (Table A3 in Appendix A). The methane concentration during resampling of this well dropped to 41 mg/L, representing a 30% decrease, but still indicative of a persistent, elevated methane concentration. Ninety percent of the wells sampled had C<sub>1</sub> concentrations <10 mg/L, and the difference between the Isoflask-corrected values and the values reported from the submersed vial method was ≤1 mg/L for those samples. The median difference in concentration between the submersed vial and the Isoflask-corrected concentrations was 0.01 mg/L. The sample with the highest C<sub>1</sub> concentration is from the Sussex area, whereas the two wells from which the

next highest C<sub>1</sub> concentrations were observed (30 and 36 mg/L) are from the Stoney Creek area. Water samples from wells completed in the Horton Group generally tend to have higher C<sub>1</sub> concentrations, while those from the Pictou Group tend to have lower concentrations (Fig. 4). Some samples from the Sussex, Mabou and Cumberland groups show C<sub>1</sub> concentrations that are equally high, or higher, than the highest observed in the Horton Group. However, samples from the Sussex and Cumberland groups show greater variability in C<sub>1</sub> concentrations between different wells and between sampling events for individual wells. This suggests that these units may exhibit more variability in hydrogeochemical conditions, as observed by Loomer *et al.* (2018) in a time-series study.

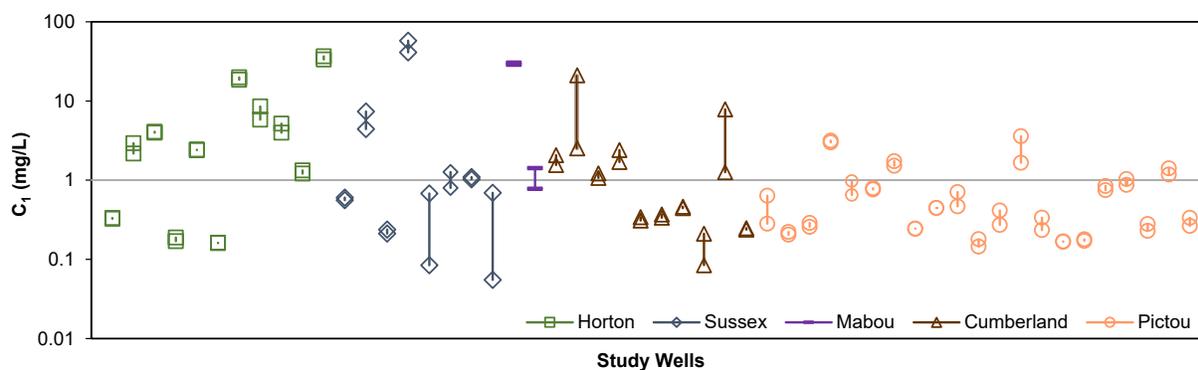
Ethane and propane were detected in 48% and 34% of the samples, with maximum concentrations of 1.9 mg/L and 0.07 mg/L, respectively. Higher weight hydrocarbons, C<sub>4</sub>–C<sub>6</sub>, were detected in two Stoney Creek area water wells: one

**Table 3.** Summary of dissolved gas concentrations from water wells (n = 52).

	C <sub>1</sub>		C <sub>2</sub>	C <sub>3</sub>
	Corrected <sup>1</sup>	Submersed vial		
Min	0.06	0.001	<0.0001	<0.0001
Max	57.58	28.88	1.44	0.07
Median	0.75	0.79	0.006	0.0003

Units in mg/L

<sup>1</sup> Equivalent IsoFlask® concentrations



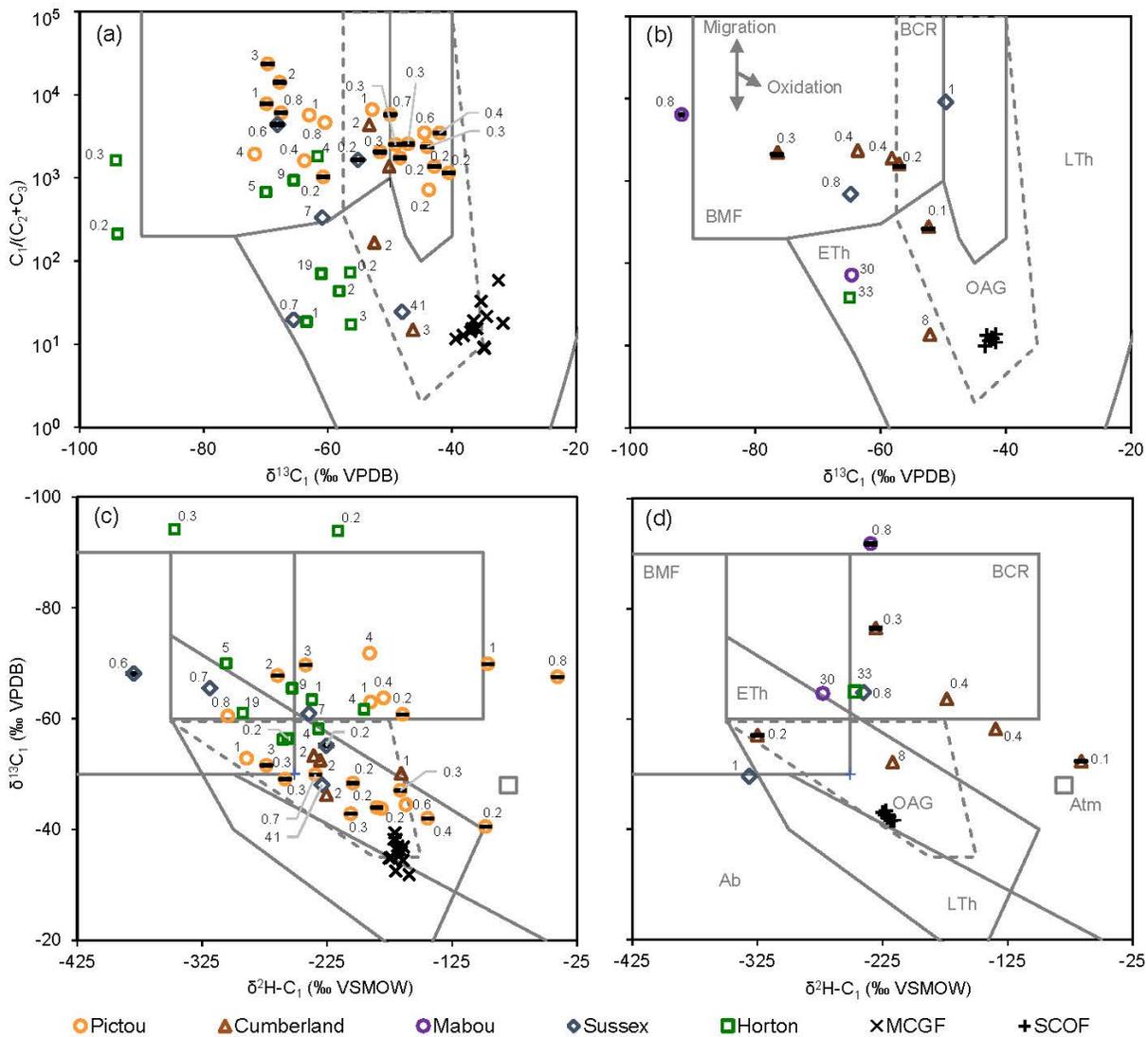
**Figure 4.** Dissolved  $C_1$  concentrations in the first and second samples from study water wells ( $n = 52$ ). The two samples for individual wells are plotted in stacked pairs; if only one symbol is shown, the difference in concentration between the two sampling events is smaller than the symbols. Samples are identified by lithostratigraphic group.

completed in Mabou Group bedrock containing 30 mg/L  $C_1$  and the other in Cumberland Group bedrock containing 1–8 mg/L  $C_1$  (Table A3 in Appendix A). Hydrocarbons from  $C_1$  to  $C_7$  have been found to be produced biogenically (D'Hondt *et al.* 2004; Whelan *et al.* 1980; Vogel *et al.* 1982), and therefore, their presence does not rule out the possibility of a biogenic source. However, their presence, coupled with the low  $C_1/(C_2+C_3)$  ratios,  $<75$ , implies a thermogenic origin.

Many researchers use molecular and isotopic discrimination diagrams to infer the  $C_1$  source (Bernard *et al.* 1976; Schoell 1983; Whiticar 1999). However, it has long been recognized that, at low concentrations, secondary isotopic fractionation related to  $C_1$  oxidation, solubility-controlled fractionation, mixing and/or diffusive transport may alter the isotopic composition from that of the original source (Fuex 1980; Whiticar 1994; Milkov and Etiope 2018). Therefore, additional lines of evidence to distinguish between possible sources are required. Researchers have utilized other geochemical data such as the noble gases (Darrah *et al.* 2014), groundwater inorganic geochemistry (Lautz *et al.* 2014), and sulphur isotopes and geochemical modeling (Humez *et al.* 2019). Here we use additional hydrocarbon compositional data coupled with geological information to support gas-origin interpretations. Source discrimination is considered unreliable when  $C_1$  concentrations are below 100 ppb in the gas phase (Whiticar 1994). The corresponding aqueous concentrations in equilibrium with such a gas phase would range from 1–5 mg/L (assuming a pressure range of 1–5 atm and a temperature range of 5–25°C). As 42 of the 52 wells sampled in this study have  $C_1$  concentrations  $<5$  mg/L, the  $C_1$  concentrations have been superimposed on the discrimination diagrams in Fig. 5 to aid assessment of the data. Twelve of the 23 samples from the baseline study areas having  $C_1$  concentrations  $\leq 1.0$  mg/L fall outside the recognized biogenic and thermogenic zones (Fig. 5a). They

also fall outside the range of values representative of mixing between biogenic and thermogenic sources, suggesting the possibility of secondary oxidation. Furthermore, inconsistencies exist between the Bernard *et al.* (1976) and Whiticar (1999) classifications of these samples (Figs. 5a, c). In the Bernard diagram, they are distinct from the MCGF. In the Whiticar diagram, the samples appear to be much closer in composition to the MCGF, but they fall within the overlapping thermogenic and oxidized biogenic zones in the diagram. All but one of the samples were collected from wells completed in Pictou Group bedrock. All Pictou Group samples that have relatively low  $C_1$  concentrations,  $<4$  mg/L, and biogenic or oxidized  $C_1$  isotopic signatures, are from the Central, Kent or Shediac study areas (Fig. 6). These areas have not been subject to ONG development and, while a thermogenic source cannot be completely ruled out, coupling the results from the two discrimination diagrams and the low  $C_1$  concentrations, the samples are thought to represent biogenic methane that has undergone partial oxidation. The apparent effects of oxidation on the isotopic composition at low  $C_1$  concentrations are consistent with the findings of Humez *et al.* (2016). Only two groundwater samples from the Stoney Creek area show the effects of  $C_1$  oxidation (Fig. 5b). One of them (completed in Sussex Group bedrock) has a high  $C_1/(C_2+C_3)$  ratio and, based on its location on the Whiticar plot, appears to represent oxidized  $C_1$  formed from methyl-type fermentation (Fig. 5d). There are also five samples in the study with  $\delta^2H-C_1$  values indicative of extreme enrichment in  $^2H$  from oxidation, approaching or surpassing the enriched  $\delta^2H-C_1$  value of  $-80\text{‰}$  commonly observed in atmospheric  $C_1$  (Whiticar 1999).

Multiple samples from water wells completed in the Horton Group show conflicting signatures, with several samples plotting within the early thermogenic zone in the Bernard diagram (Figs. 5a–b), but falling within the biogenic zones in the Whiticar diagrams (Figs. 5c–d).



**Figure 5.** Natural gas discrimination diagrams of  $\delta^{13}C-C_1$  versus  $C_1/(C_2 + C_3)$  and  $\delta^{13}C-C_1$  versus  $\delta^2H-C_1$ ; (a and c) gas samples from the MCGF (Barton 2018) and groundwater samples from the Central, Kent, Shediac and Sussex areas; (b and d) gas samples from the SCOF and groundwater samples from the Stoney Creek area. Groundwater samples are identified by geologic group and labelled with methane concentrations in mg/L. Symbols crossed by a black line indicate  $C_2$  and  $C_3$  were below detection and  $\frac{1}{2}$  the instrument detection limit (0.00005 mg/L) was used to estimate  $C_1/(C_2+C_3)$ . Gas genetic fields are based on Milkov and Etiope (2018); BMF = biogenic methyl-type fermentation, BCR = biogenic carbonate reduction, ETH = early mature thermogenic, LTh = late mature thermogenic, OAG = oil-associated gas, Ab = abiotic, Atm = atmospheric (Whiticar 1996). Polygons with dashed lines indicate oxidized biogenic.

In either classification system, the groundwaters have molecular and isotopic compositions that are distinct from the oil-associated gas and late thermogenic Horton Group signatures in the ONG fields. This suggests that alteration from migration, oxidation and/or mixing between multiple sources has occurred. Overlap between the classification zones in the recently revised Bernard and Whiticar diagrams (Milkov and Etiope 2018) further complicates interpretation.

Therefore, a biogenic influence is possible in the well with 30 mg/L  $C_1$  completed in Mabou Group bedrock. This is the well with a detectable  $C_4-C_6$  fraction and a relatively low  $C_1/(C_2+C_3)$  ratio, which is more consistent with a thermogenic origin. Hydrocarbons have been recognized in Mabou Group rock; however, analysis indicated the presence of heavy crude with no fraction  $<C_{20}$  detected (Jiang *et al.* 2016). Based on data from St. Peter and Johnson (2009),

the Horton Group is located approximately 80–90 m below the bottom of this well and may represent the source for the hydrocarbons. If the Horton Group is the source for elevated  $C_1$  concentrations in the well water, then the original thermogenic signature has been overprinted by biological activity. It is recognized that  $C_1$  is the terminal product in the anaerobic biodegradation (reduction) of a wide range of petroleum hydrocarbons, including  $C_2$  (Milkov and Dzou 2007; Scott *et al.* 1994). For the Mabou Group well and two other wells in the Stoney Creek area with  $C_2$  concentrations  $> 0.1$  mg/L, the  $\delta^{13}C_2$  values are enriched by 1–4‰ relative to gas from the SCOF (Fig. 3a). This enrichment is consistent with  $C_2$  from a residual pool after  $C_2$  reduction (Milkov and Dzou 2007). However, the corresponding  $\delta^{13}C_1$  values are depleted by 9–23‰ relative to gas from the SCOF, consistent with the effects of significant biogenesis (Chung *et al.* 1988). Therefore, methanogenesis from the reduction of  $C_2$  and higher weight hydrocarbons may explain the apparent contradictory molecular and isotopic data. The carbon isotopic indicators of  $C_2$  reduction and methanogenesis are also reflected in the hydrogen isotopes (Fig. 3b), with some minor inconsistency, which is common (Schimmelmann *et al.* 2006). During the anaerobic biodegradation of higher molecular weight hydrocarbons,  $C_1$  formation through both the acetate fermentation and  $CO_2$  reduction pathways is possible (Zengler *et al.* 1999). Methanogenesis under these circumstances may explain the apparent mix of methyl-type fermentation and carbonate reduction in the Horton and Mabou group samples from the Stoney Creek area (Fig. 5d). Together, these factors suggest that methanogenesis is occurring in the bedrock near these wells, causing an overprinting of an original thermogenic isotope signature. The methanogenesis is likely supported by the organic-rich bituminous shales of the Horton Group.

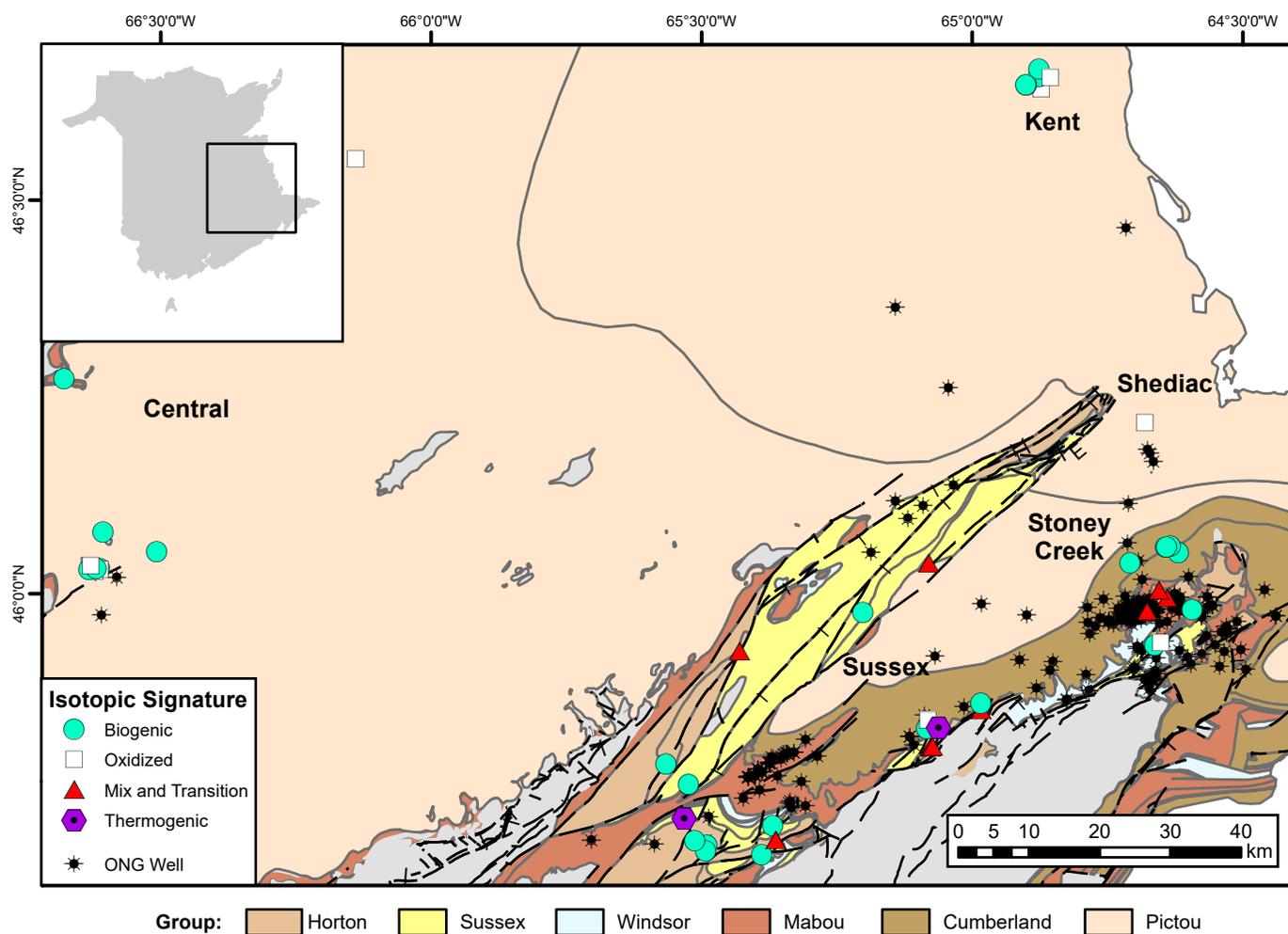
In contrast to the Horton Group, groundwater with the highest  $C_1$  concentrations from the Sussex and Cumberland groups show consistent thermogenic isotopic signatures in the Bernard and Whiticar diagrams (Fig. 5). They also plot closer to the ONG field gases, indicating a greater potential for a direct relationship between the  $C_1$  in shallow groundwater and the ONG fields. The sample with the highest  $C_1$  concentration in the study — 58 mg/L during the first sampling and 41 mg/L during the second sampling — is from a well completed in the Sussex Group and is located 3,500 m from the nearest ONG well. Provincial records indicate that the ONG well is a 378-m-deep abandoned exploration well that dates to 1913. It is not thought to represent a source of hydrocarbon gases to the water wells. Possibly a localized hydrocarbon source occurs within the Sussex Group strata; however, the well is also within 95 m of an inferred boundary with the Horton Group. Furthermore, based on data from Hinds (2008), the Horton Group is located approximately 100 m below the bedrock surface at that location. Therefore, migration from the hydrocarbon-

bearing Horton Group is the most likely source for the gases in that water well. One of the wells in Cumberland Group bedrock with  $C_1$  indicative of a thermogenic signature displayed variable concentrations, ranging from 21 to 3 mg/L, between the first and second sample events. The decrease is likely associated with the inactive water well being put into regular use after the first sample was collected. An interview with the owner of the well revealed that the well driller hit a pocket of gas at the time of drilling. The well is located near the Village of Elgin and predates unconventional ONG exploration activities in the area, which commenced in 2009 (AMEC 2014; NBDELG 2017). Therefore, the presence of thermogenic  $C_1$  in the shallow groundwater is thought to be natural. Elevated  $C_1$  concentrations have also been observed in other Cumberland Group wells located along the southeastern margin of the Moncton subbasin (Loomer *et al.* 2019). In that area, the Cumberland Group forms a thin cover directly over the Horton Group and hydrocarbon gases may be migrating upward into the overlying Cumberland Group. The preservation of a thermogenic signature in overlying Sussex and Cumberland sequences demonstrates that there are instances where  $C_1$  may be migrating from the underlying Horton Group without alteration of the original isotopic composition. Fracture-controlled transport is likely, as complex and highly conductive fracture networks have been observed in the Cumberland Group elsewhere in the Moncton subbasin (DesRoches *et al.* 2013).

Another of the Cumberland Group water wells, located within the main footprint of the SCOF (Fig. 6), displayed  $C_1$  concentrations ranging from 1 to 8 mg/L and it also had detectable  $C_2$ – $C_5$  fractions. The isotopic composition of the  $C_1$  indicates a thermogenic origin, and the hydrocarbons may be related to historic or current SCOF development activities. However, published cross-sections of the SCOF (Chowdhury *et al.* 1991; St. Peter and Johnson 2009; Park 2014) indicate that the Horton Group is located at a depth of 90 m at that location, approximately 45 m below the bottom of the water well. Therefore, the elevated  $C_1$  concentrations could also be natural, due to migration from the Horton Group. Two other water wells sampled within the footprint of the SCOF did not have  $C_1$  concentrations high enough for isotopic analyses (Loomer and MacQuarrie 2018). Given the elevated  $C_1$  concentrations observed outside the footprint of the SCOF and in other areas of the province, there is not sufficient evidence to indicate that resource extraction activities at the SCOF have caused  $C_1$  in shallow groundwater to be elevated above background levels.

## CONCLUSIONS

In this work we have compiled molecular and isotopic composition data from two regional groundwater studies and compared them to the molecular and isotopic composition



**Figure 6.** Interpreted natural gas origin based on isotopic and molecular compositional data from groundwater samples overlain on the bedrock geology of southeastern New Brunswick (NBDNR 2008; St. Peter and Johnson, 2009). Sedimentary units of the Maritimes Basin are shown in colour and other units in grey. Black lines mark fault traces. Oil and natural gas wells, including abandoned exploration wells, are shown.

data from ONG fields in New Brunswick with the objective of identifying relationships between hydrocarbons found at depth and those observed in shallow groundwater. New isotopic data from the SCOF indicate that a wet thermogenic gas was co-produced with oil in the ONG field. The gas was likely generated under conditions near the onset of the oil-gas transition zone and the  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  isotopic profiles are consistent with KIE models. The gas currently produced from the SCOF has a lower thermal maturity than that of the MCGF.

The effects of oxidation on the isotopic composition of carbon and hydrogen in aqueous  $\text{C}_1$  are apparent when  $\text{C}_1$  concentrations are low ( $\leq 1$  mg/L). Data from these low  $\text{C}_1$  samples can lead to conflicting interpretations when considering multiple source-discrimination approaches

and we found that including the  $\text{C}_1$  concentrations can help decipher the apparent contradictions. All groundwater samples from the Pictou Group have low  $\text{C}_1$  concentrations ( $\leq 4$  mg/L), and the presence of thermogenic gas in this geologic unit is considered unlikely. Elevated  $\text{C}_1$  concentrations ( $> 5$  mg/L) were observed in groundwater samples from bedrock in the Horton, Sussex, Mabou and Cumberland groups. Multiple samples from wells completed in the Horton Group also show conflicting biogenic/thermogenic signatures despite gases from the Horton Group having different and distinct thermogenic signatures at depth. The possible influence of biogenic activity is also evident in a well completed in the Mabou Group. Conflicting molecular,  $\text{C}_1$ - $\text{C}_6$ , and isotopic,  $\delta^{13}\text{C}_1$  and  $\delta^{13}\text{C}_2$  data from these wells suggest that biological activity has

overprinted an original thermogenic source in near-surface Horton Group bedrock. Therefore, the isotopic composition of dissolved hydrocarbon gases in shallow groundwater may be subject to considerable alteration not only at low  $C_1$  concentrations, but also at elevated concentrations. This has major implications for the understanding of baseline methane occurrences should ONG development proceed in the Maritimes Basin. Future baseline study design and interpretation should be evaluated within this context. Multiple lines of evidence are required for reliable interpretations concerning hydrocarbon origins.

Thermogenic isotopic signatures occur in samples with elevated  $C_1$  concentrations from several locations where bedrock of Sussex, Mabou or Cumberland group directly overlies the Horton Group. This suggests  $C_1$  may be migrating through natural pathways from the Horton Group without significant alteration of the isotopic composition. Fracture-controlled transport is the most likely explanation.

#### ACKNOWLEDGEMENTS

Funding for this project was provided by the New Brunswick Energy Institute (of which Tom Al was a member of the scientific advisory council) and by Natural Resources Canada, as part of the project *Assessing methane emissions from legacy fossil resource development and methane mitigation potential in Atlantic Canada*, led by Grant Wach of Dalhousie University. Scholarship funding for Diana Loomer has been provided by the Natural Sciences and Engineering Research Council of Canada, the University of New Brunswick, the O'Brien Foundation and Engineers and Geoscientists New Brunswick.

We would like to acknowledge the well owners who volunteered for this study and the valuable contributions of Ian Bragdon (field and laboratory support), Heather Loomer (field and data management support), Dennis Connor, Christine Chase, Jessica Leblanc, Thomas Lewey and Brian Nason (field support). We appreciate the technical support of Diane Botelho (Research and Productivity Council, Fredericton) and Steve Hinds and Tom Howard (New Brunswick Department of Energy and Resource Development). We would also like to express our appreciation to the anonymous reviewers for helping us improve the manuscript.

#### REFERENCES

- Acadian Securities. 2007. Contact exploration: high-impact Atlantic Canadian Oil & Gas exposure at bargain-basement price. Equity Research Initiating Coverage, 21 p. URL <[http://www.stocksandspeculations.com/i/pdf/162a%20CEX\\_Initiating%20Coverage\\_11-13-07.pdf](http://www.stocksandspeculations.com/i/pdf/162a%20CEX_Initiating%20Coverage_11-13-07.pdf)> 13, November 2007.
- AMEC. 2014. Phased environmental impact assessment PHASE III: natural gas exploration at Elgin sub-basin, Elgin, New Brunswick. Report prepared by AMEC Environment and Infrastructure, a division of AMEC Americas Limited, Fredericton, New Brunswick, TE131057.
- Barton, D. 2018. Chemical and stable isotopic characterization of geofluids from an unconventional natural gas field in New Brunswick, Canada. Unpublished M.Sc. thesis, University of Ottawa, Ottawa, Ontario, Canada, 73 p.
- Bernard, B.B., Brooks, J.M., and Sackett, W.M. 1976. Natural gas seepage in the Gulf of Mexico. *Earth and Planetary Science Letters*, 31, pp. 48–54. [https://doi.org/10.1016/0012-821X\(76\)90095-9](https://doi.org/10.1016/0012-821X(76)90095-9)
- Berner, U., Faber, E., Scheeder, G., and Panten, D. 1995. Primary cracking of algal and land plant kerogens: kinetic models of isotope variations in methane, ethane and propane. *Chemical Geology*, 126, pp. 233–245. [https://doi.org/10.1016/0009-2541\(95\)00120-4](https://doi.org/10.1016/0009-2541(95)00120-4)
- Burruss, R.C. and Laughrey, C.D. 2010. Carbon and hydrogen isotopic reversals in deep basin gas: evidence for limits to the stability of hydrocarbons. *Organic Geochemistry*, 41, pp. 1285–1296. <https://doi.org/10.1016/j.orggeochem.2010.09.008>
- Chowdhury, A.H. 1991. Sedimentology, diagenesis and organic chemistry of the Albert Formation, Moncton subbasin, New Brunswick, Canada. Unpublished Ph.D. thesis, University of New Brunswick, Fredericton, New Brunswick, 249 p.
- Chowdhury, A.H., Fowler, M.G., and Noble, J.P.A. 1991. Petroleum geochemistry and geology of the Albert Formation Moncton subbasin, New Brunswick, Canada. *Bulletin of Canadian Petroleum Geology*, 39, pp. 315–331.
- Chung, H.M., Gormly, J.R., and Squires, R.M. 1988. Origin of gaseous hydrocarbons in subsurface environments: theoretical considerations of carbon isotope distribution. *Chemical Geology*, 71, pp. 97–103. [https://doi.org/10.1016/0009-2541\(88\)90108-8](https://doi.org/10.1016/0009-2541(88)90108-8)
- Corridor Resources Inc. 2019. Annual information report for the year ended December 31, 2018. Report dated March 27, 2019, 48 p.
- D'Hondt, S., Jørgensen, B.B., Miller, D.J., Batzke, A., Blake, R., Cragg, B.A., Cypionka, H., Dickens, G.R., Ferdelman, T., Hinrichs, K.-U., Holm, N.G., Mitterer, R., Spivack, A., Wang, G., Bekins, B., Engelen, B., Ford, K., Gettemy, G., Rutherford, S.D., *et al.* 2004. Distributions of microbial activities in deep subseafloor sediments. *Science*, 306, pp. 2216–2221. <https://doi.org/10.1126/science.1101155>
- Darrah, T.H., A. Vengosh, R.B. Jackson, N.R. Warner and R.J. Poreda. 2014. Noble gases identify the mechanisms of fugitive gas contamination in drinking-water wells overlying the Marcellus and Barnett shales. *Proceedings*

- of the National Academy of Sciences, 111, pp. 14076–14081. <https://doi.org/10.1073/pnas.1322107111>
- DesRoches, A.J., Butler, K.E., and Pelkey, S. 2013. Influence of fracture anisotropy and lithological heterogeneity on wellfield response in a fluvial sandstone aquifer of the Carboniferous Moncton subbasin, Canada. *Hydrogeology Journal*, 21, pp. 559–572. <https://doi.org/10.1007/s10040-012-0931-6>
- Foley, S.L. 1989. Geology of the Stoney Creek Oil and Gas Field, and its implications regarding the tectonic evolution of the eastern Moncton subbasin, New Brunswick. Department of Natural Resources and Energy, Minerals and Energy Division, Geoscience Report 89–1, 77 p.
- Fuex, A.N. 1980. Experimental evidence against an appreciable isotopic fractionation of methane during migration. *Physics and Chemistry of the Earth*, 12, pp. 725–732. [https://doi.org/10.1016/0079-1946\(79\)90153-8](https://doi.org/10.1016/0079-1946(79)90153-8)
- Harkness, J.S., Darrach, T.H., Warner, N.R., Whyte, C.J., Moore, M.T., Millot, R., Kloppmann, W., Jackson, R.B. and Vengosh, A. 2017. The geochemistry of naturally occurring methane and saline groundwater in an area of unconventional shale gas development. *Geochimica et Cosmochimica Acta*, 208, pp. 302–334. <https://doi.org/10.1016/j.gca.2017.03.039>
- Harkness, J.S., Swana, K., Eymold, W.K., Miller, J., Murray, R., Talma, S., Whyte, C.J., Moore, M.T., Maletic, E.L., Vengosh, A. and Darrach, T.H. 2018. Pre-drill groundwater geochemistry in the Karoo Basin, South Africa. *Groundwater*, 56, pp. 187–203. <https://doi.org/10.1111/gwat.12635>
- Hinds, S. 2008. Geology of the Apohaqui area (NTS 21 H/12h). Kings County. New Brunswick. New Brunswick Department of Natural Resources: Minerals and Policy and Planning Division. Plate 2008-10 (revised 2009), scale 1:20 000.
- Hinds, S.J. and St. Peter, C.J. 2006. Stratigraphy and structure of the Moncton subbasin in the Urney–Waterford area, Maritimes Basin, New Brunswick: implications for the McCully Natural Gas Field. *In* Geological investigations in New Brunswick for 2005. *Edited by* G.L. Martin, New Brunswick Department of Natural Resources; Minerals, Policy and Planning Division, Mineral Resource Report 2006-3, pp.73–102.
- Humez, P., Mayer, B., Nightingale, M., Becker, V., Kingston, A., Taylor, S., Bayegnak, G. Millot, R., and Kloppmann, W. 2016. Redox controls on methane formation, migration and fate in shallow aquifers. *Hydrology and Earth System Sciences*, 20, pp. 2759–2777. <https://doi.org/10.5194/hess-20-2759-2016>
- Humez, P., Osselin, F., Kloppmann, W., and Mayer, B. 2019. A geochemical and multi-isotope modeling approach to determine sources and fate of methane in shallow groundwater above unconventional hydrocarbon reservoirs. *Journal of Contaminant Hydrology*, 226, 103525. <https://doi.org/10.1016/j.jconhyd.2019.103525>
- Jiang, C., Lavoie, D. and Rivard, C. 2016. An organic geochemical investigation of the Carboniferous Mabou Group intersected by groundwater wells in McCully gas field, Southern New Brunswick — its hydrocarbon source potential and character. Geological Survey of Canada, Open File 8071, 34 p. <https://doi.org/10.4095/298803>
- Keighley, D. 2008. A lacustrine shoreface succession in the Albert Formation, Moncton Basin, New Brunswick. *Bulletin of Canadian Petroleum Geology*. 56, pp. 235–258. <https://doi.org/10.2113/gscpgbull.56.4.235>
- Lautz, L.K., G.D. Hoke, Z. Lu, D.I. Siegel, K. Christian, J.D. Kessler and N.G. Teale. 2014. Using discriminant analysis to determine sources of salinity in shallow groundwater prior to hydraulic fracturing. *Environmental Science & Technology*, 48, pp. 9061–9069. <https://doi.org/10.1021/es502244v>
- Loomer, D.B. and MacQuarrie, K.T.B. 2018. The occurrence of methane and other hydrocarbon gases in private water supply wells near the Stoney Creek oil and natural gas field, New Brunswick. New Brunswick Department of Energy and Resource Development, Open File 2018-3, 28 p.
- Loomer, D., MacQuarrie, K., Bragdon, I., Connor, D., Loomer, H., Leblanc, J., and Nason, B. 2016. A baseline assessment of private well water quality in areas of potential shale gas development in New Brunswick: final report. Prepared for the New Brunswick Energy Institute, Fredericton, New Brunswick. August 2016, 85 p.
- Loomer, D.B., MacQuarrie, K.T.B., Al, T.A., Bragdon, I.K., and Loomer, H.A. 2018. Temporal variability of dissolved methane and inorganic water chemistry in private well water in New Brunswick, Canada. *Applied Geochemistry*, 94, pp. 53–66. <https://doi.org/10.1016/j.apgeochem.2018.05.003>
- Loomer, D.B., MacQuarrie, K.T.B., and Al, T.A. 2019. Using permutational and multivariate statistics to understand inorganic well water chemistry and the occurrence of methane in groundwater, southeastern New Brunswick, Canada. *Science of the Total Environment*, 675, pp. 667–678. <https://doi.org/10.1016/j.scitotenv.2019.04.256>
- Martin, G.L. 2003. Gesner’s dream: the trials and tribulations of early mining in New Brunswick. *Canadian Institute of Mining, Metallurgy and Petroleum*, Fredericton, 328 p.
- McIntosh, J.C., Grasby, S.E., Hamilton, S.M., and Osborn, S.G. 2014. Origin, distribution and hydrogeochemical controls on methane occurrences in shallow aquifers, southwestern Ontario, Canada. *Applied Geochemistry*, 50, pp. 37–52. <https://doi.org/10.1016/j.apgeochem.2014.08.001>
- McMahon, P.B., Barlow, J.R.B., Engle, M.A., Belitz, K., Ging, P.B., Hunt, A.G., Jurgens, B.C., Kharaka, Y.K., Tollett, R.W., and Kresse, T.M. 2017. Methane and benzene in drinking-water wells overlying the Eagle Ford, Fayetteville, and Haynesville shale hydrocarbon production areas.

- Environmental Science & Technology, 51, pp. 6727–6734. <https://doi.org/10.1021/acs.est.7b00746>
- Milkov, A.V. and Dzou, L. 2007. Geochemical evidence of secondary microbial methane from very slight biodegradation of undersaturated oils in a deep hot reservoir. *Geology*, 35, pp. 455–458. <https://doi.org/10.1130/G23557A.1>
- Milkov, A.V. and Etiope, G. 2018. Revised genetic diagrams for natural gases based on a global dataset of >20,000 samples. *Organic Geochemistry*, 125, pp. 109–120. <https://doi.org/10.1016/j.orggeochem.2018.09.002>
- Molofsky, L.J., Richardson, S.D., Gorody, A.W., Baldassare, F., Black, J.A., McHugh, T.E., and Connor, J.A. 2016. Effect of different sampling methodologies on measured methane concentrations in groundwater samples. *Groundwater*, 54, pp. 669–680. <https://doi.org/10.1111/gwat.12415>
- Moritz, A., Hélie, J.-F., Pinti, D.L., Larocque, M., Barnette, D., Retailleau, S., Lefebvre, R., and Gélinas, Y. 2015. Methane baseline concentrations and sources in shallow aquifers from the shale gas-prone region of the St. Lawrence Lowlands (Quebec, Canada). *Environmental Science & Technology*, 49, pp. 4765–4771. <https://doi.org/10.1021/acs.est.5b00443>
- NBDELG. 2017. New Brunswick Department of Environment and Local Government Online Well Log System. URL <<https://www.elgegl.gnb.ca/0375-0001/>> 10, June 2017.
- NBDERD. 2019. New Brunswick Department of Natural Resources and Energy Development Lidar Products. Data retrieved in 2019.
- NBDNR. 2008. Bedrock geology of New Brunswick. New Brunswick Department of Energy and Mines, Minerals Policy and Planning Division Map NR-1 2008 Ed, scale 1:500 000. Revised December 2008 and online digital Bedrock Geology Maps 1:20 000 scale.
- Ni, Y., Ma, Q., Ellis, G.S., Dai, J., Katz, B., Zhang, S., and Tang, Y. 2011. Fundamental studies on kinetic isotope effect (KIE) of hydrogen isotope fractionation in natural gas systems. *Geochimica et Cosmochimica Acta*, 75, pp. 2696–2707. <https://doi.org/10.1016/j.gca.2011.02.016>
- Orlen. 2019. ORLEN Upstream operations in Canada. URL <<http://www.orlenupstream.pl/EN/Projects/Pages/Operations-in-Canada.aspx>> 22, May 2019.
- Park, A.F. 2014. Shale gas in New Brunswick: geological background. *In* Shale gas in New Brunswick: towards a better understanding. Edited by R. Saillant. Canadian Institute for Research on Public Policy and Public Administration, Moncton, pp. 79–133.
- Schimmelmann, A., Sessions, A.L., and Mastalerz, M. 2006. Hydrogen isotopic (D/H) composition of organic matter during diagenesis and thermal maturation. *Annual Review of Earth and Planetary Science*, 34, pp. 501–533. <https://doi.org/10.1146/annurev.earth.34.031405.125011>
- Schoell, M. 1983. Genetic characterization of natural gases. *American Association of Petroleum Geologists Bulletin*, 67, pp. 2225–2238. <https://doi.org/10.1306/AD46094A-16F7-11D7-8645000102C1865D>
- Scott, A.R., Kaiser, W.R., and Ayers, W.B. 1994. Thermogenic and secondary biogenic gases, San Juan Basin, Colorado and New Mexico — implications for coalbed gas producibility. *American Association of Petroleum Geologists Bulletin*, 78, pp. 1186–1209. <https://doi.org/10.1306/A25FEAA9-171B-11D7-8645000102C1865D>
- Sharma, S., Mulder, M.L., Sack, A., Schroeder, K., and Hammack, R. 2014. Isotope approach to assess hydrologic connections during Marcellus Shale drilling. *Groundwater*, 52, pp. 424–433. <https://doi.org/10.1111/gwat.12083>
- St. Peter, C. 2000. Oil shales and oil and natural gas in New Brunswick: historical and current industry-related activities. New Brunswick Department of Natural Resources and Energy, Minerals and Energy Division, Information Circular 2000-5, 14 p.
- St. Peter, C.J. and Johnson, S.C. 2009. Stratigraphy and structural history of the late Paleozoic Maritimes Basin in southeastern New Brunswick, Canada. New Brunswick Department of Natural Resources, Minerals, Policy and Planning Division, Memoir 3, 348 p.
- Tilley, B. and Muehlenbachs, K. 2013. Isotope reversals and universal stages and trends of gas maturation in sealed, self-contained petroleum systems. *Chemical Geology*, 339, pp. 194–204. <https://doi.org/10.1016/j.chemgeo.2012.08.002>
- Vengosh, A., Jackson, R.B., Warner, N., Darrah, T.H., and Kondash, A. 2014. A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. *Environmental Science & Technology*, 48, pp. 8334–8348. <https://doi.org/10.1021/es405118y>
- Vidic, R.D., Brantley, S.L., Vandenbossche, J.M., Yoxheimer, D., and Abad, J.D. 2013. Impact of shale gas development on regional water quality. *Science*, 340 (6134), pp. 1235009–1–9. <https://doi.org/10.1126/science.1235009>
- Vogel, T.M., Oremland, R.S., and Kvenvolden, K.A. 1982. Low-temperature formation of hydrocarbon gases in San Francisco Bay sediment. *Chemical Geology*, 37, pp. 289–298. [https://doi.org/10.1016/0009-2541\(82\)90084-5](https://doi.org/10.1016/0009-2541(82)90084-5)
- Wang, X., Liu, W., Shi, B., Zhang, Z., Xu, Y., and Zheng, J. 2015. Hydrogen isotope characteristics of thermogenic methane in Chinese sedimentary basins. *Organic Geochemistry*, 83–84, pp. 178–189. <https://doi.org/10.1016/j.orggeochem.2015.03.010>
- Whelan, J.K., Hunt, J.M., and Berman, J. 1980. Volatile C<sub>1</sub>-C<sub>7</sub> organic compounds in surface sediments from Walvis Bay. *Geochimica et Cosmochimica Acta*, 44, pp. 1767–1785. [https://doi.org/10.1016/0016-7037\(80\)90227-6](https://doi.org/10.1016/0016-7037(80)90227-6)
- Whiticar, M.J. 1994. Correlation of natural gases with their sources. *In* The petroleum system—from source to

- trap. *Edited by* L.B. Magoon and W.G. Dow. American Association of Petroleum Geologists Memoir 60, pp. 261–283. <https://doi.org/10.1306/M60585C16>
- Whiticar, M.J. 1996. Stable isotope geochemistry of coals, humic kerogens and related natural gases. *International Journal of Coal Geology*, 32, pp. 191–215. [https://doi.org/10.1016/S0166-5162\(96\)00042-0](https://doi.org/10.1016/S0166-5162(96)00042-0)
- Whiticar, M.J. 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chemical Geology*, 161, pp. 291–314. [https://doi.org/10.1016/S0009-2541\(99\)00092-3](https://doi.org/10.1016/S0009-2541(99)00092-3)
- Wilson, P. and White, J.C. 2006. Tectonic evolution of the Moncton Basin, New Brunswick, eastern Canada: new evidence from field and sub-surface data. *Bulletin of Canadian Petroleum Geology*, 54, pp. 319–336. <https://doi.org/10.2113/gscpgbull.54.4.319>
- Zengler, K., Richnow, H.H., Rosselló-Mora, R., Michaelis, W., and Widdel, F. 1999. Methane formation from long-chain alkanes by anaerobic microorganisms. *Nature*, 402, pp. 266–269. <https://doi.org/10.1038/45777>

*Editorial responsibility: Robert A. Fensome*

## APPENDIX A

**TableA1.** Dissolved gas concentrations in field blank samples.

Sample	Methane	Ethane	Propane
	mg/L		
2DOA008	0.0001	<0.0001	<0.0001
DOA063	0.0001	<0.0001	<0.0001
DOA084	0.0001	<0.0001	<0.0001
DOA121	0.0001	<0.0001	0.0001
DOA128	0.0001	<0.0001	0.0001
KEN005	0.0001	<0.0001	<0.0001
KEN117	0.0002	<0.0001	<0.0001
KEN306	0.0001	<0.0001	<0.0001
KEN406	0.0003	<0.0001	<0.0001
KEN413	0.0001	<0.0001	<0.0001
SHE016	0.0002	<0.0001	<0.0001
SHE052	0.0001	<0.0001	<0.0001
SUS077	0.0002	<0.0001	<0.0001
SUS572	0.0001	<0.0001	<0.0001
SUS646	0.0002	<0.0001	<0.0001
SUS654	0.0001	<0.0001	<0.0001
SUS687	0.0001	<0.0001	<0.0001
SCK007	0.0002	<0.0001	<0.0001
SCK036	0.0001	<0.0001	<0.0001
SCK055	0.0002	<0.0001	<0.0001
SCK063 <sup>1</sup>	0.0002	<0.0001	<0.0001

<sup>1</sup> Sample collected in an IsoFlask®.

## APPENDIX A

**Table A2.** Results of field replicate analyses for dissolved hydrocarbon gas concentrations.

Sample	Methane	Ethane	Propane	Sample	Methane	Ethane	Propane	Sample	Methane	Ethane	Propane
	mg/L				mg/L				mg/L		
SUS205	2.0881	0.1286	<0.0001	SUS094	0.0001	<0.0001	<0.0001	SUS048	0.0001	<0.0001	0.0011
SUS206	1.9058	0.116	<0.0001	SUS095	0.0001	<0.0001	0.00018	SUS049	0.0001	<0.0001	<0.0001
SUS207	1.8659	0.1137	<0.0001	SUS096	0.0001	<0.0001	0.00017	SUS050	0.0001	<0.0001	<0.0001
<b>Mean</b>	<b>1.9533</b>	<b>0.1194</b>	<b>NA</b>	<b>Mean</b>	<b>0.0001</b>	<b>NA</b>	<b>0.0002</b>	<b>Mean</b>	<b>0.0001</b>	<b>NA</b>	<b>0.0004</b>
<b>σ</b>	<b>0.1185</b>	<b>0.008</b>	<b>NA</b>	<b>σ</b>	<b>0</b>	<b>NA</b>	<b>0</b>	<b>σ</b>	<b>0</b>	<b>NA</b>	<b>0.0006</b>
<b>RSD</b>	<b>6.10%</b>	<b>6.70%</b>	<b>NA</b>	<b>RSD</b>	<b>0.00%</b>	<b>NA</b>	<b>4.00%</b>	<b>RSD</b>	<b>0.00%</b>	<b>NA</b>	<b>151.60%</b>
SUS511	0.0605	0.0011	<0.0001	SUS192	6.8226	0.0214	<0.0001	SUS502	0.0561	<0.0001	<0.0001
SUS512	0.0645	0.0012	<0.0001	SUS193	6.3927	0.0205	<0.0001	SUS503	0.0565	<0.0001	<0.0001
SUS513	0.0717	0.0013	<0.0001	SUS194	6.4374	0.0212	<0.0001	SUS504	0.0496	<0.0001	<0.0001
<b>Mean</b>	<b>0.0656</b>	<b>0.0012</b>	<b>NA</b>	<b>Mean</b>	<b>6.5509</b>	<b>0.021</b>	<b>NA</b>	<b>Mean</b>	<b>0.0541</b>	<b>NA</b>	<b>NA</b>
<b>σ</b>	<b>0.0057</b>	<b>0.0001</b>	<b>NA</b>	<b>σ</b>	<b>0.2364</b>	<b>0.0005</b>	<b>NA</b>	<b>σ</b>	<b>0.0039</b>	<b>NA</b>	<b>NA</b>
<b>RSD</b>	<b>8.70%</b>	<b>8.30%</b>	<b>NA</b>	<b>RSD</b>	<b>3.60%</b>	<b>2.20%</b>	<b>NA</b>	<b>RSD</b>	<b>7.20%</b>	<b>NA</b>	<b>NA</b>
SUS177	0.0031	<0.0001	<0.0001	SUS072	0.0002	<0.0001	<0.0001	SUS032	1.5934	<0.0001	0.00054
SUS178	0.0033	<0.0001	<0.0001	SUS073	0.0002	<0.0001	<0.0001	SUS033	1.9583	<0.0001	0.00071
SUS179	0.003	<0.0001	<0.0001	SUS074	0.0002	<0.0001	<0.0001	<b>Mean</b>	<b>1.7759</b>	<b>NA</b>	<b>0.0006</b>
<b>Mean</b>	<b>0.0031</b>	<b>NA</b>	<b>NA</b>	<b>Mean</b>	<b>0.0002</b>	<b>NA</b>	<b>NA</b>	<b>RD</b>	<b>0.1453</b>	<b>NA</b>	<b>0.1923</b>
<b>σ</b>	<b>0.0002</b>	<b>NA</b>	<b>NA</b>	<b>σ</b>	<b>0</b>	<b>NA</b>	<b>NA</b>				
<b>RSD</b>	<b>4.90%</b>	<b>NA</b>	<b>NA</b>	<b>RSD</b>	<b>0.00%</b>	<b>NA</b>	<b>NA</b>				
SUS148	2.3753	<0.0001	0.00047	SUS160	14.1425	0.228	0.00195	SUS557	0.0449	<0.0001	<0.0001
SUS149	2.4904	0.0002	0.00041	SUS161	13.6677	0.2223	0.00185	SUS558	0.0834	<0.0001	<0.0001
SUS150	2.521	0.0002	0.00046	SUS162	14.3736	0.2299	0.00196	SUS559	0.0275	<0.0001	<0.0001
<b>Mean</b>	<b>2.4622</b>	<b>0.0002</b>	<b>0.0004</b>	<b>Mean</b>	<b>14.0613</b>	<b>0.2267</b>	<b>0.0019</b>	<b>Mean</b>	<b>0.0519</b>	<b>NA</b>	<b>NA</b>
<b>σ</b>	<b>0.0769</b>	<b>0.0001</b>	<b>0</b>	<b>σ</b>	<b>0.3599</b>	<b>0.004</b>	<b>0.0001</b>	<b>σ</b>	<b>0.0286</b>	<b>NA</b>	<b>NA</b>
<b>RSD</b>	<b>3.10%</b>	<b>57.70%</b>	<b>7.20%</b>	<b>RSD</b>	<b>2.60%</b>	<b>1.70%</b>	<b>3.20%</b>	<b>RSD</b>	<b>55.10%</b>	<b>NA</b>	<b>NA</b>
SUS681	0.5199	0.0004	<0.0001	SHE027	0.0223	<0.0001	<0.0001	SHE017	0.0004	<0.0001	<0.0001
SUS682	1.4116	0.0013	<0.0001	SHE028	0.0233	<0.0001	<0.0001	SHE018	0.0004	<0.0001	<0.0001
SUS683	2.1783	0.0021	<0.0001	SHE029	0.0231	<0.0001	<0.0001	SHE019	0.0004	<0.0001	<0.0001
<b>Mean</b>	<b>1.3699</b>	<b>0.0013</b>	<b>NA</b>	<b>Mean</b>	<b>0.0229</b>	<b>NA</b>	<b>NA</b>	<b>Mean</b>	<b>0.0004</b>	<b>NA</b>	<b>NA</b>
<b>σ</b>	<b>0.83</b>	<b>0.0009</b>	<b>NA</b>	<b>σ</b>	<b>0.0005</b>	<b>NA</b>	<b>NA</b>	<b>σ</b>	<b>0</b>	<b>NA</b>	<b>NA</b>
<b>RSD</b>	<b>60.60%</b>	<b>67.10%</b>	<b>NA</b>	<b>RSD</b>	<b>2.30%</b>	<b>NA</b>	<b>NA</b>	<b>RSD</b>	<b>0.00%</b>	<b>NA</b>	<b>NA</b>
SHE054	0.6356	<0.0001	5.00E-05	KEN368	0.2762	<0.0001	<0.0001	KEN041	0.0056	<0.0001	0.00052
SHE055	0.6513	<0.0001	5.00E-05	KEN369	0.1955	<0.0001	<0.0001	KEN042	0.0058	<0.0001	0.00064
SHE056	0.6949	<0.0001	5.00E-05	<b>Mean</b>	<b>0.2359</b>	<b>NA</b>	<b>NA</b>	KEN043	0.007	<0.0001	0.0006
<b>Mean</b>	<b>0.6606</b>	<b>NA</b>	<b>0.0001</b>	<b>σ</b>	<b>0.0571</b>	<b>NA</b>	<b>NA</b>	<b>Mean</b>	<b>0.0061</b>	<b>NA</b>	<b>0.0006</b>
<b>σ</b>	<b>0.0307</b>	<b>NA</b>	<b>0</b>	<b>RSD</b>	<b>24.20%</b>	<b>NA</b>	<b>NA</b>	<b>σ</b>	<b>0.0008</b>	<b>NA</b>	<b>0.0001</b>
<b>RSD</b>	<b>4.70%</b>	<b>NA</b>	<b>0.00%</b>					<b>RSD</b>	<b>12.30%</b>	<b>NA</b>	<b>10.40%</b>
KEN107	0.0294	<0.0001	<0.0001	KEN061	0.0001	<0.0001	<0.0001	KEN015	0.0013	<0.0001	<0.0001
KEN108	0.0268	<0.0001	<0.0001	KEN062	0.0001	<0.0001	<0.0001	KEN016	0.0013	<0.0001	<0.0001
KEN109	0.0269	<0.0001	<0.0001	KEN063	0.0001	<0.0001	<0.0001	KEN017	0.0012	<0.0001	<0.0001
<b>Mean</b>	<b>0.0277</b>	<b>NA</b>	<b>NA</b>	<b>Mean</b>	<b>0.0001</b>	<b>NA</b>	<b>NA</b>	<b>Mean</b>	<b>0.0013</b>	<b>NA</b>	<b>NA</b>
<b>σ</b>	<b>0.0015</b>	<b>NA</b>	<b>NA</b>	<b>σ</b>	<b>0</b>	<b>NA</b>	<b>NA</b>	<b>σ</b>	<b>0.0001</b>	<b>NA</b>	<b>NA</b>
<b>RSD</b>	<b>5.30%</b>	<b>NA</b>	<b>NA</b>	<b>RSD</b>	<b>0.00%</b>	<b>NA</b>	<b>NA</b>	<b>RSD</b>	<b>4.00%</b>	<b>NA</b>	<b>NA</b>

## APPENDIX A

Table A2. Continued.

Sample	Methane	Ethane	Propane	Sample	Methane	Ethane	Propane	Sample	Methane	Ethane	Propane
mg/L			mg/L			mg/L					
KEN072	0.0001	<0.0001	<0.0001	KEN125	0.0002	<0.0001	<0.0001	DOA054	0.0072	<0.0001	<0.0001
KEN073	<0.0005	<0.0001	<0.0001	KEN126	0.0001	<0.0001	<0.0001	DOA055	0.0067	<0.0001	<0.0001
KEN074	<0.0005	<0.0001	<0.0001	KEN127	0.0001	<0.0001	<0.0001	DOA056	0.0069	<0.0001	<0.0001
<b>Mean</b>	<b>0.0001</b>	<b>NA</b>	<b>NA</b>	<b>Mean</b>	<b>0.0001</b>	<b>NA</b>	<b>NA</b>	<b>Mean</b>	<b>0.0069</b>	<b>NA</b>	<b>NA</b>
<b><math>\sigma</math></b>	<b>0</b>	<b>NA</b>	<b>NA</b>	<b><math>\sigma</math></b>	<b>0.0001</b>	<b>NA</b>	<b>NA</b>	<b><math>\sigma</math></b>	<b>0.0003</b>	<b>NA</b>	<b>NA</b>
<b>RSD</b>	<b>43.30%</b>	<b>NA</b>	<b>NA</b>	<b>RSD</b>	<b>43.30%</b>	<b>NA</b>	<b>NA</b>	<b>RSD</b>	<b>3.60%</b>	<b>NA</b>	<b>NA</b>
DOA133	0.0004	<0.0001	<0.0001	DOA160	0.439	<0.0001	<0.0001	DOA122	0.0001	<0.0001	<0.0001
DOA134	0.0003	<0.0001	<0.0001	DOA161	0.4572	<0.0001	<0.0001	DOA123	0.0001	<0.0001	<0.0001
DOA135	0.0002	<0.0001	0.0002	DOA162	0.4486	<0.0001	<0.0001	DOA124	0.0002	<0.0001	<0.0001
<b>Mean</b>	<b>0.0003</b>	<b>NA</b>	<b>0.0001</b>	<b>Mean</b>	<b>0.4483</b>	<b>NA</b>	<b>NA</b>	<b>Mean</b>	<b>0.0001</b>	<b>NA</b>	<b>NA</b>
<b><math>\sigma</math></b>	<b>0.0001</b>	<b>NA</b>	<b>0</b>	<b><math>\sigma</math></b>	<b>0.0091</b>	<b>NA</b>	<b>NA</b>	<b><math>\sigma</math></b>	<b>0.0001</b>	<b>NA</b>	<b>NA</b>
<b>RSD</b>	<b>33.30%</b>	<b>NA</b>	<b>0.00%</b>	<b>RSD</b>	<b>2.00%</b>	<b>NA</b>	<b>NA</b>	<b>RSD</b>	<b>43.30%</b>	<b>NA</b>	<b>NA</b>
DOA010	0.4318	<0.0001	<0.0001	DOA032	0.0141	<0.0001	<0.0001	2DOA010	0.0008	<0.0001	<0.0001
DOA011	0.4849	<0.0001	<0.0001	DOA033	0.0139	<0.0001	<0.0001	2DOA011	0.0007	<0.0001	<0.0001
DOA012	0.501	<0.0001	<0.0001	DOA034	0.0138	<0.0001	<0.0001	2DOA012	0.0007	<0.0001	<0.0001
<b>Mean</b>	<b>0.4726</b>	<b>NA</b>	<b>NA</b>	<b>Mean</b>	<b>0.0139</b>	<b>NA</b>	<b>NA</b>	<b>Mean</b>	<b>0.0007</b>	<b>NA</b>	<b>NA</b>
<b><math>\sigma</math></b>	<b>0.0362</b>	<b>NA</b>	<b>NA</b>	<b><math>\sigma</math></b>	<b>0.0002</b>	<b>NA</b>	<b>NA</b>	<b><math>\sigma</math></b>	<b>0.0001</b>	<b>NA</b>	<b>NA</b>
<b>RSD</b>	<b>7.70%</b>	<b>NA</b>	<b>NA</b>	<b>RSD</b>	<b>1.10%</b>	<b>NA</b>	<b>NA</b>	<b>RSD</b>	<b>7.90%</b>	<b>NA</b>	<b>NA</b>
DOA139	0.0002	<0.0001	<0.0001	DOA086	0.0001	<0.0001	<0.0001	DOA097	0.0001	<0.0001	<0.0001
DOA140	0.0002	<0.0001	<0.0001	DOA087	0.0001	<0.0001	<0.0001	DOA098	0.0001	<0.0001	<0.0001
DOA141	0.0002	<0.0001	<0.0001	DOA088	0	<0.0001	<0.0001	DOA099	0.0001	<0.0001	<0.0001
<b>Mean</b>	<b>0.0002</b>	<b>NA</b>	<b>NA</b>	<b>Mean</b>	<b>0.0001</b>	<b>NA</b>	<b>NA</b>	<b>Mean</b>	<b>0.0001</b>	<b>NA</b>	<b>NA</b>
<b><math>\sigma</math></b>	<b>0</b>	<b>NA</b>	<b>NA</b>	<b><math>\sigma</math></b>	<b>0.0001</b>	<b>NA</b>	<b>NA</b>	<b><math>\sigma</math></b>	<b>0</b>	<b>NA</b>	<b>NA</b>
<b>RSD</b>	<b>0.00%</b>	<b>NA</b>	<b>NA</b>	<b>RSD</b>	<b>86.60%</b>	<b>NA</b>	<b>NA</b>	<b>RSD</b>	<b>0.00%</b>	<b>NA</b>	<b>NA</b>
SCK049	0.0269	<0.0001	<0.0001	SCK023	0.0078	<0.0001	<0.0001	SCK056 <sup>1</sup>	29.366	0.8091	0.0352
SCK050	0.0369	<0.0001	<0.0001	SCK024	0.0071	<0.0001	<0.0001	SCK057 <sup>1</sup>	29.645	0.8361	0.0367
SCK051	0.0433	<0.0001	<0.0001	SCK025	0.0057	<0.0001	<0.0001	<b>Mean</b>	<b>29.5055</b>	<b>0.8226</b>	<b>0.036</b>
<b>Mean</b>	<b>0.0357</b>	<b>NA</b>	<b>NA</b>	<b>Mean</b>	<b>0.0069</b>	<b>NA</b>	<b>NA</b>	<b>RD</b>	<b>0.70%</b>	<b>2.30%</b>	<b>2.80%</b>
<b><math>\sigma</math></b>	<b>0.0083</b>	<b>NA</b>	<b>NA</b>	<b><math>\sigma</math></b>	<b>0.0011</b>	<b>NA</b>	<b>NA</b>				
<b>RSD</b>	<b>23.20%</b>	<b>NA</b>	<b>NA</b>	<b>RSD</b>	<b>15.60%</b>	<b>NA</b>	<b>NA</b>				

" $\sigma$ " means standard deviation, "NA" means not applicable.

<sup>1</sup> Samples collected in IsoFlasks.

## APPENDIX A

**Table A3.** Dissolved hydrocarbon gas concentrations and isotopic compositions in groundwater.

Sample	Well	Group	IsoFlask*			Corrected <sup>1</sup>		Submersed vial			$\delta^2\text{H}$	$\delta^{13}\text{C}$	$\delta^2\text{H}$	$\delta^{13}\text{C}$				
			C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>1</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>1</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub>					
											mg/L				‰			
SUS132	W-020	Horton	-	-	-	0.33	0.31	0.0001	nd	-	-	-	-					
SUS181	W-020	Horton	-	-	-	0.33	0.32	0.0002	nd	-347	-94.2	-	-					
SUS167	W-023	Cumberland	-	-	-	2.07	2.15	0.0174	0.0004	-	-	-	-					
SUS604	W-023	Cumberland	-	-	-	1.55	1.63	0.0104	0.0001	-231	-52.5	-	-					
SUS168	W-026	Cumberland	-	-	-	21.09	14.69	1.4407	0.0032	-	-	-	-					
SUS188	W-026	Cumberland	-	-	-	2.53	2.59	0.1836	0.0015	-226	-46.3	-	-					
SUS053	W-038	Horton	-	-	-	2.17	2.24	0.1411	nd	-	-	-	-					
SUS183	W-038	Horton	-	-	-	2.92	2.96	0.1876	0.0002	-260	-56.3	-	-					
SUS164	W-052	Sussex	-	-	-	0.6	0.62	0.0001	0.0003	-	-	-	-					
SUS190	W-052	Sussex	-	-	-	0.56	0.58	nd	nd	-380	-68.1	-	-					
SUS012	W-057	Horton	-	-	-	3.98	3.9	nd	nd	-	-	-	-					
SUS139	W-057	Horton	-	-	-	4.09	3.99	0.0018	0.0005	-195	-61.7	-	-					
SUS087	W-060	Horton	-	-	-	0.17	0.13	0.0019	nd	-	-	-	-					
SUS154	W-060	Horton	-	-	-	0.19	0.16	0.0022	nd	-256	-56.4	-	-					
SUS013	W-062	Cumberland	-	-	-	1.21	1.28	nd	nd	-	-	-	-					
SUS152	W-062	Cumberland	-	-	-	1.07	1.13	0.0008	nd	-166	-50.1	-	-					
SUS159	W-069	Sussex	-	-	-	4.42	4.27	0.012	nd	-	-	-	-					
SUS192	W-069	Sussex	-	-	-	7.34	6.55	0.021	nd	-240	-60.9	-	-					
SUS102	W-074	Horton	-	-	-	2.4	2.46	0.0644	0.0003	-	-	-	-					
SUS151	W-074	Horton	-	-	-	2.42	2.48	0.0611	nd	-232	-58.2	-	-					
SUS084	W-081	Sussex	-	-	-	0.21	0.18	nd	0.0003	-	-	-	-					
SUS143	W-081	Sussex	-	-	-	0.24	0.21	nd	nd	-226	-55.2	-	-					
SUS122	W-085	Horton	-	-	-	0.16	0.13	0.0004	0.0002	-	-	-	-					
SUS182	W-085	Horton	-	-	-	0.16	0.12	0.0002	0.0005	-217	-93.9	-	-					
SUS011	W-104	Sussex	-	-	-	57.58	28.88	1.1184	nd	-	-	-	-					
SUS138	W-104	Sussex	-	-	-	41.11	23.21	1.0152	0.0024	-229	-48	-	-					
SUS032	W-112	Cumberland	-	-	-	1.69	1.78	nd	0.0006	-	-	-	-					
SUS148	W-112	Cumberland	-	-	-	2.4	2.46	0.0001	0.0004	-236	-53.3	-	-					
SUS160	W-120	Horton	-	-	-	19.85	14.06	0.2267	0.0019	-	-	-	-					
SUS195	W-120	Horton	-	-	-	18.59	13.41	0.2026	0.0017	-293	-61.1	-	-					
SUS035	W-129	Horton	-	-	-	5.8	5.39	0.0062	0.0003	-	-	-	-					
SUS141	W-129	Horton	-	-	-	8.52	7.39	0.0082	0.0003	-253	-65.5	-	-					
SUS062	W-143	Horton	-	-	-	3.97	3.89	0.0051	nd	-	-	-	-					
SUS145	W-143	Horton	-	-	-	5.17	4.89	0.0075	0.0003	-306	-70	-	-					
SUS184	W-144	Horton	-	-	-	1.33	1.4	0.041	nd	-	-	-	-					
SUS187	W-144	Horton	-	-	-	1.21	1.28	0.0365	nd	-237	-63.5	-	-					
SUS043	W-152	Sussex	-	-	-	0.08	0.04	nd	nd	-	-	-	-					
SUS186	W-152	Sussex	-	-	-	0.68	0.71	nd	nd	-319	-65.5	-	-					
SHE047	W-167	Pictou	-	-	-	0.28	0.26	nd	0.0001	-	-	-	-					
SHE054	W-167	Pictou	-	-	-	0.64	0.66	nd	0.0001	-162	-44.5	-	-					
KEN069	W-193	Pictou	-	-	-	0.22	0.19	nd	nd	-	-	-	-					
KEN116	W-193	Pictou	-	-	-	0.21	0.18	nd	nd	-206	-42.8	-	-					
KEN099	W-194	Pictou	-	-	-	0.29	0.27	nd	nd	-	-	-	-					
KEN368	W-194	Pictou	-	-	-	0.26	0.24	nd	nd	-185	-44	-	-					

## APPENDIX A

Table A3. Continued.

Sample	Well	Group	IsoFlask®			Corrected <sup>1</sup>		Submersed vial			$\delta^2\text{H}$	$\delta^{13}\text{C}$	$\delta^2\text{H}$	$\delta^{13}\text{C}$			
			C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>1</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>1</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub>				
										mg/L				‰			
KEN027	W-208	Pictou	-	-	-	3.15	3.16	nd	nd	-	-	-	-				
KEN120	W-208	Pictou	-	-	-	2.99	3.02	nd	nd	-242	-69.7	-	-				
KEN098	W-240	Pictou	-	-	-	0.65	0.67	nd	nd	-	-	-	-				
KEN129	W-240	Pictou	-	-	-	0.97	1.03	nd	nd	-96	-69.9	-	-				
KEN122	W-273	Pictou	-	-	-	0.79	0.83	nd	nd	-	-	-	-				
KEN132	W-273	Pictou	-	-	-	0.76	0.8	nd	nd	-40	-67.5	-	-				
KEN009	W-277	Pictou	-	-	-	1.52	1.6	nd	nd	-	-	-	-				
KEN123	W-277	Pictou	-	-	-	1.73	1.81	nd	nd	-265	-67.8	-	-				
2DOA003	W-321	Pictou	-	-	-	0.24	0.22	nd	nd	-	-	-	-				
DOA109	W-321	Pictou	-	-	-	0.24	0.22	nd	nd	-204	-48.4	-	-				
DOA103	W-322	Pictou	-	-	-	0.45	0.45	nd	nd	-	-	-	-				
DOA160	W-322	Pictou	-	-	-	0.44	0.45	nd	nd	-145	-42	-	-				
DOA010	W-334	Pictou	-	-	-	0.47	0.47	nd	nd	-	-	-	-				
DOA113	W-334	Pictou	-	-	-	0.71	0.74	nd	nd	-234	-49.9	-	-				
DOA053	W-340	Pictou	-	-	-	0.14	0.11	nd	nd	-	-	-	-				
DOA118	W-340	Pictou	-	-	-	0.18	0.15	nd	nd	-98	-40.5	-	-				
DOA022	W-341	Pictou	-	-	-	0.27	0.25	0.0001	0.0004	-	-	-	-				
DOA112	W-341	Pictou	-	-	-	0.41	0.41	0.0002	0.0001	-180	-63.7	-	-				
DOA100	W-350	Pictou	-	-	-	1.66	1.74	0.0009	nd	-	-	-	-				
DOA117	W-350	Pictou	-	-	-	3.59	3.56	0.0019	nd	-191	-71.8	-	-				
DOA036	W-387	Pictou	-	-	-	0.23	0.21	nd	nd	-	-	-	-				
DOA110	W-387	Pictou	-	-	-	0.34	0.33	nd	nd	-259	-49.1	-	-				
DOA035	W-396	Pictou	-	-	-	0.17	0.13	nd	nd	-	-	-	-				
DOA119	W-396	Pictou	-	-	-	0.17	0.13	nd	nd	-164	-60.7	-	-				
2DOA025	W-399	Pictou	-	-	-	0.17	0.14	nd	0.0001	-181	-43.7	-	-				
DOA136	W-399	Pictou	-	-	-	0.18	0.15	nd	0.0001	-	-	-	-				
DOA006	W-404	Pictou	-	-	-	0.75	0.78	nd	nd	-	-	-	-				
DOA111	W-404	Pictou	-	-	-	0.85	0.89	nd	0.0001	-304	-60.5	-	-				
DOA045	W-407	Pictou	-	-	-	0.87	0.92	0.0001	nd	-	-	-	-				
DOA116	W-407	Pictou	-	-	-	1.03	1.09	0.0001	nd	-190	-63	-	-				
DOA067	W-421	Pictou	-	-	-	0.23	0.2	nd	nd	-	-	-	-				
DOA115	W-421	Pictou	-	-	-	0.28	0.26	nd	nd	-274	-51.6	-	-				
DOA125	W-422	Pictou	-	-	-	1.41	1.49	nd	0.0001	-	-	-	-				
DOA155	W-422	Pictou	-	-	-	1.18	1.24	nd	0.0001	-289	-52.8	-	-				
DOA082	W-434	Pictou	-	-	-	0.26	0.24	nd	nd	-	-	-	-				
DOA114	W-434	Pictou	-	-	-	0.33	0.32	nd	nd	-166	-47.1	-	-				
SCK004	SCK-003	Horton	36.27	1.9305	0.0001	36.66	21.51	1.2487	0.0001	-	-	-	-				
SCK064	SCK-003	Horton	35.21	1.8935	0.0002	33.32	20.17	1.185	0.0001	-247	-65	-204	-34.2				
SCK010 <sup>2</sup>	SCK-004	Mabou	27.87	0.8287	0.0196	28.69	18.22	0.5731	0.0144	-	-	-	-				
SCK057 <sup>3</sup>	SCK-004	Mabou	29.51	0.8226	0.036	30.42	18.96	0.5469	0.0244	-273	-64.6	-167	-34.9				
SCK008	SCK-005	Cumberland	0.4	nd	nd	0.34	0.33	nd	nd	-	-	-	-				
SCK048	SCK-005	Cumberland	-	-	-	0.31	0.29	nd	nd	-230	-76.5	-	-				
SCK006	SCK-006	Cumberland	0.39	0.0001	nd	0.34	0.33	0.0001	nd	-	-	-	-				
SCK061	SCK-006	Cumberland	-	-	-	0.37	0.36	0.0001	nd	-135	-58.2	-	-				

## APPENDIX A

Table A3. Continued.

Sample	Well	Group	IsoFlask®			Corrected <sup>1</sup>	Submersed vial			$\delta^2\text{H}$	$\delta^{13}\text{C}$	$\delta^2\text{H}$	$\delta^{13}\text{C}$				
			C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>1</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>1</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub>				
										mg/L				‰			
SCK005	SCK-007	Cumberland	0.57	0.0001	nd	0.46	0.47	0.0001	nd	-	-	-	-				
SCK062	SCK-007	Cumberland	-	-	-	0.44	0.45	0.0001	nd	-174	-63.7	-	-				
SCK009	SCK-008	Cumberland	0.23	nd	nd	0.21	0.18	nd	nd	-	-	-	-				
SCK051	SCK-008	Cumberland	-	-	-	0.08	0.04	nd	nd	-66	-52.3	-	-				
SCK011 <sup>3</sup>	SCK-010	Cumberland	1.98	0.0937	0.0101	1.26	1.33	0.0665	0.0075	-	-	-	-				
SCK054 <sup>3</sup>	SCK-010	Cumberland	-	-	-	7.84	6.91	0.475	0.0684	-217	-52.2	-178	-32.9				
SCK018	SCK-014	Cumberland	0.23	nd	nd	0.25	0.22	nd	nd	-	-	-	-				
SCK047	SCK-014	Cumberland	-	-	-	0.24	0.21	nd	nd	-325	-57.1	-	-				
SCK032	SCK-025	Windsor	0.78	nd	nd	0.69	0.72	nd	nd	-	-	-	-				
SCK058	SCK-025	Windsor	-	-	-	0.06	0	0.0001	nd	-	-	-	-				
SCK034	SCK-033	Mabou	1.63	0.0001	nd	1.41	1.49	0.0001	nd	-	-	-	-				
SCK053	SCK-033	Mabou	-	-	-	0.78	0.82	nd	nd	-234	-91.8	-	-				
SCK043	SCK-039	Sussex	1.56	0.0025	nd	1.27	1.34	0.0023	nd	-	-	-	-				
SCK059	SCK-039	Sussex	-	-	-	0.8	0.84	0.0013	nd	-240	-64.8	-	-				
SCK046	SCK-040	Sussex	1.25	nd	nd	1.03	1.08	nd	nd	-	-	-	-				
SCK060	SCK-040	Sussex	-	-	-	1.09	1.16	nd	nd	-331	-49.6	-	-				

Sample ID prefix indicates study area: DOA = Central, KEN = Kent, SHE = Shediac, SCK = Stoney Creek and SUS = Sussex

$\delta^2\text{H}$  is measured relative to VSMOW and  $\delta^{13}\text{C}$  is measured relative to VPDB; "nd" mean not detected; "-" means not measured

<sup>1</sup> C<sub>1</sub> concentrations measured in the vials have been converted to equivalent IsoFlask® concentrations.

<sup>2</sup> C<sub>4</sub> – C<sub>6</sub> hydrocarbons detected but not quantified.

<sup>3</sup> C<sub>4</sub> – C<sub>6</sub> hydrocarbons detected but not quantified.

APPENDIX B

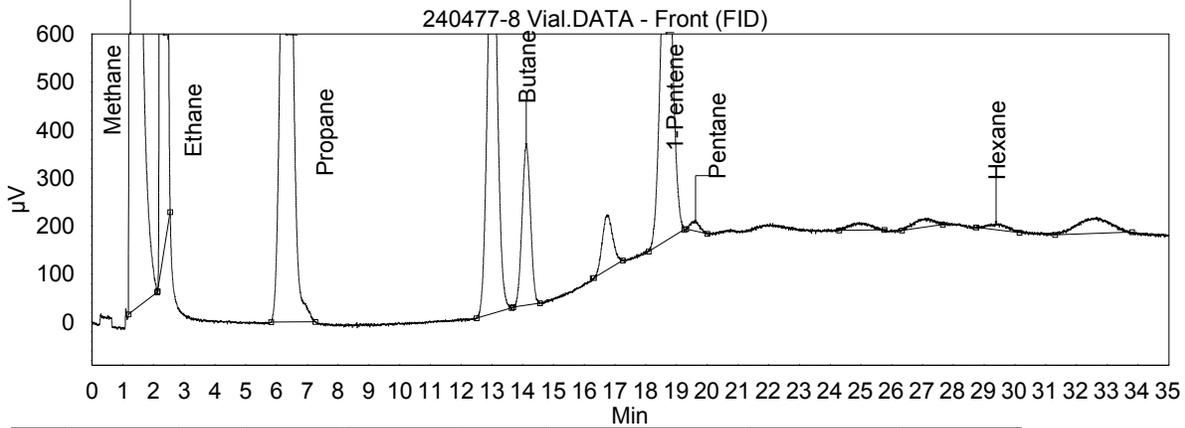
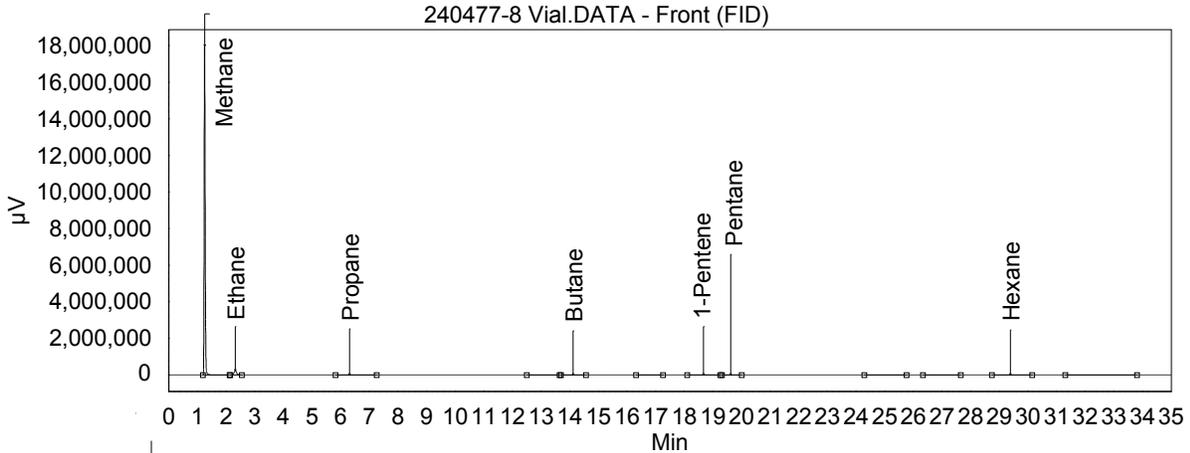
Example chromatographs for samples with detectable >C<sub>3</sub> fractions.  
 Samples ID: SCK010

System : 450 Methane  
 Method : C1-C6 Gas Analysis CompiPal  
 User : RPC  
 Calibration Curve: Calibrations\2017\Dissolved Gas in Water  
 June 13 2017, Date Modified: 6/13/2017 4:24:20 PM

**Chromatogram : 240477-8 Vial**

Room Temperature: 22.90 Headspace: 4.80

Acquired : 7/6/2017 6:28:04 PM Processed : 7/13/2017 10:55:17 AM Printed : 7/13/2017 10:55:21 AM



Peak Results

Name	Time [Min]	Quantity [ppmv]	Height [µV]	Area [µV.Min]	Analyte in Headspace [mg/L]	Analyte in Water [m/L]	Total Analyte [mg/L]
Methane	1.25	167928.02	17974387.6	724007.9	14.3182	3.9025	18.2207
Ethylene	2.02	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Ethane	2.33	2617.74	223268.8	23930.4	0.4184	0.1548	0.5731
Propylene	5.77	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Propane	6.32	47.05	1634.9	641.1	0.0110	0.0033	0.0144
UNKNOWN	13.02	0.00	903.5	330.9	0.0000	0.0000	0.0000
1-Butene	13.52	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Butane	14.12	24.54	334.1	105.8	0.0000	0.0000	0.0000
UNKNOWN	16.74	0.00	115.4	44.6	0.0000	0.0000	0.0000
1-Pentene	18.67	74.75	731.4	322.3	0.0000	0.0000	0.0000
Pentane	19.62	1.56	19.7	6.7	0.0000	0.0000	0.0000
UNKNOWN	24.94	0.00	16.7	11.3	0.0000	0.0000	0.0000
UNKNOWN	27.09	0.00	19.1	12.8	0.0000	0.0000	0.0000
1-Hexene	28.06	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Hexane	29.39	1.98	14.9	8.5	0.0000	0.0000	0.0000
UNKNOWN	32.66	0.00	33.4	39.8	0.0000	0.0000	0.0000
Total		170695.64	18201479.5	749462.0			

APPENDIX B

Example chromatographs for samples with detectable >C<sub>3</sub> fractions.

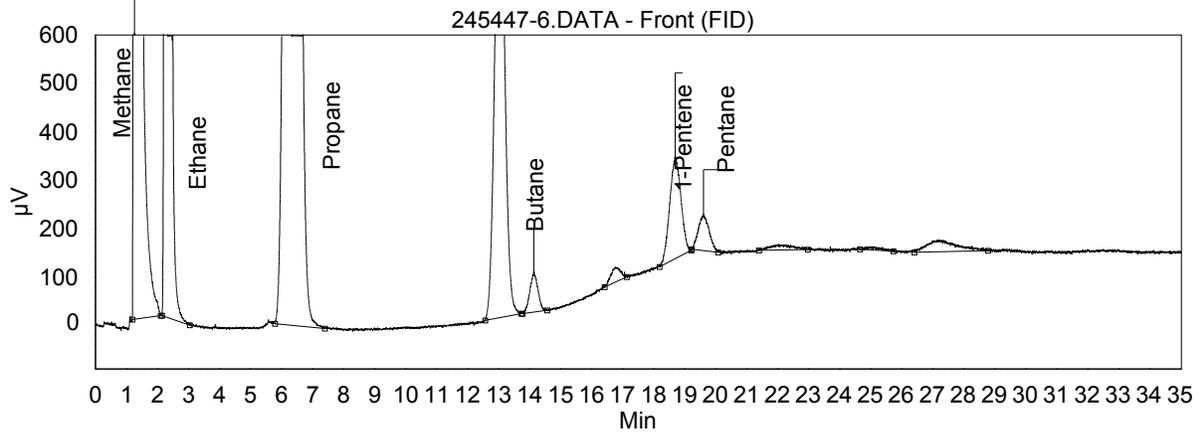
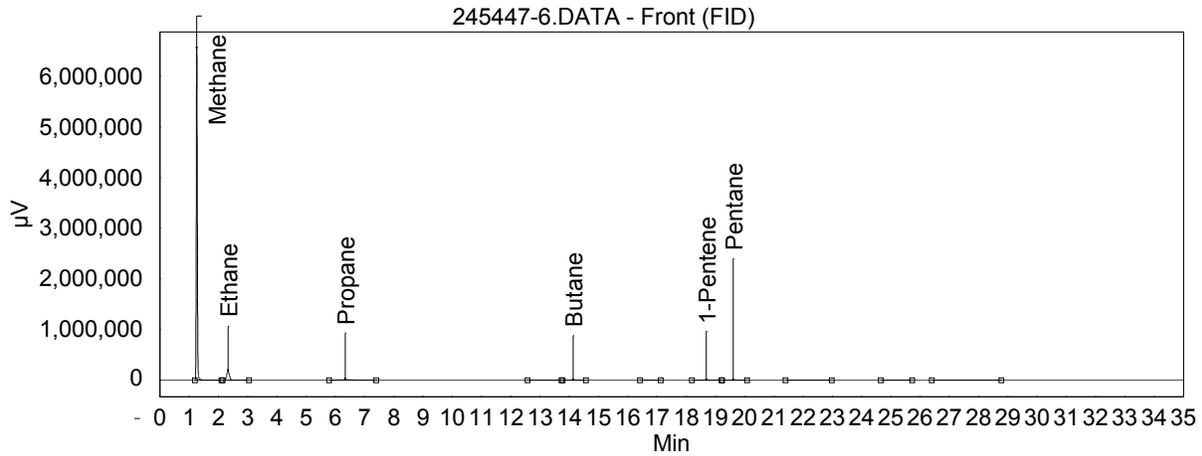
System : 450 Methane  
 Method : C1-C6 Gas Analysis CompiPal  
 User : RPC  
 Calibration Curve: Calibrations\2017\Dissolved Gas in Water  
 August 15 2017, Date Modified: 8/15/2017 4:05:36 PM

Sample ID: SCK054

Room Temperature: 22.90 Headspace: 4.80

**Chromatogram : 245447-6**

Acquired : 8/21/2017 6:28:36 PM Processed : 8/22/2017 1:06:56 PM Printed : 8/23/2017 12:24:23 PM



Peak Results	Name	Time [Min]	Quantity [ppmv]	Height [µV]	Area [µV.Min]	Analyte in Headspace [mg/L]	Analyte in Water [m/L]	Total Analyte [mg/L]
		Methane	1.26	63724.66	6547526.5	259278.9	5.4334	1.4809
	Ethylene	2.02	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Ethane	2.33	2169.47	180605.1	19130.5	0.3467	0.1283	0.4750
	Propylene	5.77	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Propane	6.33	224.33	7649.3	2954.8	0.0526	0.0159	0.0684
	UNKNOWN	13.04	0.00	1020.4	375.0	0.0000	0.0000	0.0000
	1-Butene	13.52	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Butane	14.13	5.98	79.6	24.3	0.0000	0.0000	0.0000
	UNKNOWN	16.77	0.00	28.5	11.2	0.0000	0.0000	0.0000
	1-Pentene	18.69	21.64	207.3	88.0	0.0000	0.0000	0.0000
	Pentane	19.60	7.29	71.7	29.7	0.0000	0.0000	0.0000
	UNKNOWN	21.99	0.00	11.4	8.8	0.0000	0.0000	0.0000
	UNKNOWN	25.04	0.00	6.3	3.1	0.0000	0.0000	0.0000
	UNKNOWN	27.14	0.00	25.0	26.8	0.0000	0.0000	0.0000
	1-Hexene	28.06	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Hexane	29.55	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	<b>Total</b>		<b>66153.38</b>	<b>6737231.0</b>	<b>281931.2</b>			