Temporal variations of methane concentration and isotopic composition in groundwater of the St. Lawrence Lowlands, eastern Canada

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Abstract

Dissolved methane concentrations in shallow groundwater are known to vary both spatially and temporally. However, the extent of these variations is poorly documented and this knowledge is critical for distinguishing natural fluctuations from anthropogenic impacts stemming from oil and gas activities. This issue was addressed as part of a groundwater research project aiming to assess the risk of shale gas development for groundwater quality over a 500 km^2 area in the St. Lawrence Lowlands (Quebec, Canada). A specific study was carried out to define the natural variability of methane concentrations and carbon and hydrogen isotope ratios in groundwater, as dissolved methane is naturally ubiquitous in aquifers of this area. Monitoring was carried out over a period of up to 2.5 years in seven monitoring wells. Results showed that for a given well, using the same sampling depth and technique, methane concentrations can vary over time from 2.5 to 6 times relative to the lowest recorded value. Methane isotopic composition, which is a useful tool to distinguish gas origin, was found to be stable for most wells, but varied significantly over time in the two wells where methane concentrations are the lowest. The use of concentration ratios, as well as isotopic composition of methane and dissolved inorganic carbon (DIC) helped unravel the processes responsible for these variations. This study indicates that both methane concentrations and isotopic composition, as well as DIC isotopes, should be regularly monitored over at least one year to establish their potential natural variations prior to hydrocarbon development.

Keywords: methane concentrations and stable isotopes, groundwater monitoring, St. Lawrence Lowlands (eastern Canada)

1 Introduction

Dissolved methane concentration in groundwater is known to vary spatially according to various natural factors, including the geological context, groundwater geochemistry and residence time, and topography (e.g. Molofsky et al. 2013; McIntosh et al. 2014; Moritz et al. 2015; Siegel et al. 2015; Humez et al. 2016), but it is also known to vary temporally (e.g. Gorody 2012; Coleman and McElreath 2012; Humez et al. 2015; Smith et al. 2016, Currell et al., 2017; Sherwood et al., 2017; see section A1 in the Appendix for an in-depth review). Many authors in the last decade have stressed the need for long-term monitoring data of dissolved methane concentrations and isotopic composition (e.g. Hirsche and Mayer 2009; Gorody 2012; Jackson et al. 2013; Jackson and Heagle 2016; Ryan et al. 2015). Knowledge of these natural variations to establish baseline methane concentrations and isotopic composition prior to hydrocarbon exploration and exploitation is of utmost importance to support the evaluation of potential impacts of these deep activities on shallow aquifers used for water supply.

Ryan et al. (2015) discussed the issue of long-term methane monitoring data, suggesting that before environmental impacts can be assessed in a meaningful way, the origin of natural methane, its distribution, and temporal and spatial variability must be fully characterized and understood. Jackson et al. (2013) identified an urgent need for baseline geochemical mapping that would include time series sampling from a sufficient network of groundwater monitoring wells to fill current science gaps related to hydrocarbon development. Hirsche and Mayer (2009) and Cheung and Mayer (2009) have underlined that knowledge of the extent of natural variability of concentrations and isotopic composition of methane, higher alkanes, and CO_2 in groundwater prior to sub-surface industrial activities has to be a pre-requisite for a quantifiable assessment of potential contamination cases.

Several authors (Hirsche and Mayer 2009; Coleman and McElreath 2012; Humez et al. 2015; Smith et al. 2016) documented that different wells do not exhibit the same degree of variability in methane concentrations in a study area and that short-term variations may even be very significant for a given well. Dusseault and Jackson (2014) stated that hydrogeologists must consider the fact that concentrations may considerably vary over time when designing the monitoring plan for sampling groundwater in observation wells. These authors were, in particular, referring to potential seepage from faulty oil and gas well casings that can lead to irregular “gas slugs” (i.e., the coalescence of numerous bubbles), but it could be inferred that the latter could also perhaps be applicable to methane migration through preferential pathways in hydrogeological systems.

Multiple environmental factors and anthropogenic activities are known to impact methane concentrations. For instance, dissolved methane variations in aquifers are assumed to be related to precipitation cycles, barometric pressure changes, aquifer mixing and microbial processes, as well as pumping, irrigation and industrial activity (Gorody et al. 2005; 2012; Hirsche and Mayer 2009; Coleman and McElreath 2012). The sampling technique may also impact the concentrations measured in samples, especially for groundwater with high concentrations of dissolved methane. Molofsky et al. (2016b) showed that the use of a “closed” groundwater sampling system provided higher methane concentrations than the traditional bottle-filling methods above 20 mg/L due to degassing occurring in “open” sampling systems. For example, the Isoflask® disposable containers, which correspond to one of the best known closed systems, sample both dissolved and free gas and can be directly connected to instruments allowing the analysis of both phases.

Very few studies have included the monitoring of several wells for methane concentrations and isotopic composition over time. The present paper documents this type of monitoring carried out over a 2.5 year period in seven open borehole monitoring wells having very different conditions. This study is part of a larger project studying the presence of potential natural pathways for upward migration of fluids close to a shale gas well in an area with no past or current shale gas production. It aims to document the temporal variability of methane concentrations and isotopic composition, and to provide an example of how to carry out groundwater monitoring to assess such variability.

2 Description of the study area

The 500-km^2 study area where our monitoring wells were drilled is located in the St. Lawrence Lowlands, about 65 km south-west of Quebec City, Quebec, Canada, and is centered around Saint-Édouard (Fig. 1). This is a rural area with a few small municipalities. Twenty-eight shale gas exploration wells were drilled in the St. Lawrence Lowlands between 2006 and 2010, targeting the Upper Ordovician Utica Shale which covers over 10 000 km^2 (Lavoie et al. 2014). Among these wells, two (one vertical and one horizontal) were drilled in the Saint-Édouard area by Talisman Energy in 2009. The horizontal well was hydraulically fractured in early 2010. All shale gas exploration activities stopped in 2010 when the Quebec *de facto* hydraulic fracturing moratorium came into force. The St. Lawrence Lowlands and the Saint-Édouard study area can thus be considered in a pre-development condition relative to oil and gas exploitation in general. Methane concentrations and isotopes in groundwater from supply or monitoring wells in the study area thus provide indications of the natural temporal variability of pre-development baseline conditions.

The topography of the study area is relatively flat, being around 90 masl at well F2 in the Appalachian piedmont (the most southerly observation well), to about 30 masl close to the

St. Lawrence River, 17 km to the north. Total precipitation in this region is on average 1170 mm/y and monthly mean temperatures vary from -11.7 to 19.8 ˚C (from the Government of Canada website: www.climate.weather.gc.ca).

3.1 Geological context

In southern Quebec, a Middle Cambrian – Upper Ordovician sedimentary succession is preserved in the St. Lawrence Platform (Lavoie, 2008). In its northeastern domain, such as in the Saint-Édouard area, the surface geology consists only of Upper Ordovician clastic-dominated units. Figure 1 shows that the study area comprises the Lotbinière, Nicolet and Pontgravé formations of the St. Lawrence Platform (autochtonous domain), as well as the Les Fonds Formation of the parautochthonous domain (Lavoie et al. 2014 and 2016). The Lotbinière and Les Fonds formations consist predominantly of black, locally very calcareous, shale interbedded with subordinate thin siltstone strata, whereas the Nicolet Formation is mainly composed of grey and non-calcareous silty shale (Lavoie et al. 2016). These Upper Ordovician shales were deposited in a fast subsiding tectonic foredeep with the carbonates being produced from a coeval but distant shallow marine carbonate platform that was backstepping on the craton (Lavoie and Asselin, 1998; Lavoie, 2008). The Utica Shale is 2-km deep in the Saint-Édouard Talisman A267/A275 wells, but shallows to about 500 m underneath the Lotbinière Formation at the northwest limit of the study area (Lavoie et al. 2016) (Fig. 1). It has long been known that shales of the basal section of the Lorraine

Group contain hydrocarbons, but in lower concentration than in the Utica Shale (Lavoie et al. 2008).

The regional NE-trending Chambly-Fortierville open syncline is present in the central part of the study area (Fig. 1). The St. Lawrence Platform is cut by the Rivière Jacques-Cartier normal fault, which limits to the southeast, the Lotbinière Formation. The Aston SE-verging and Logan NW-verging thrust faults in the southeastern part of the study area limit the tectonized parautochthonous domain where St. Lawrence Platform-related units such as Les Fonds Formation are present (Fig. 1). Between the Rivière Jacques-Cartier and Aston faults, the Upper Ordovician succession consists of the Nicolet Formation. The Appalachian domain begins southeast of Logan's Line.

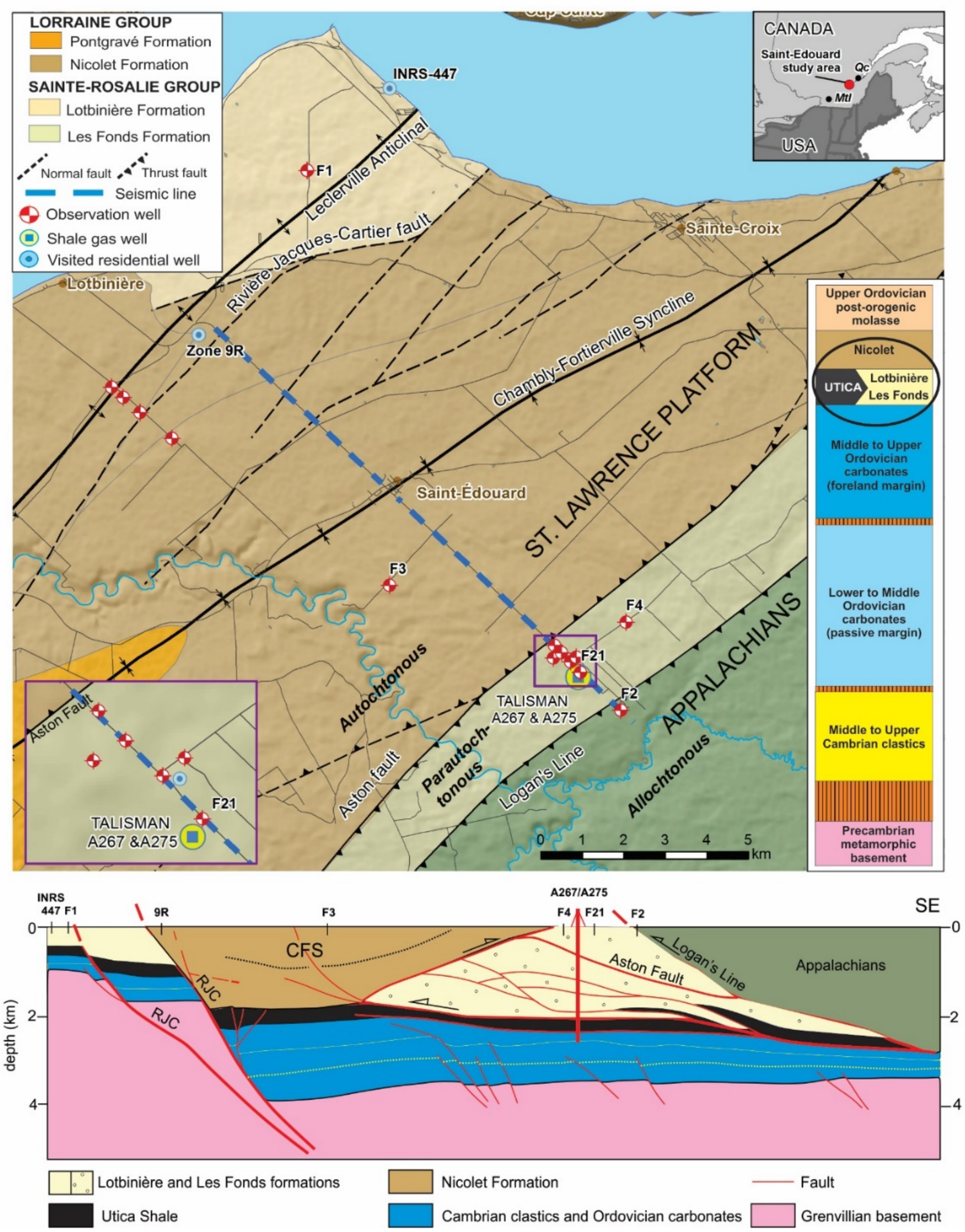

Fig. 1 Location of the study area and the monitoring wells discussed in this study (those showing a name), the dashed blue line locates a seismic section, the interpretation of which is shown at the bottom (from Lavoie et al., 2016). The position of monitoring wells discussed in this study are projected on the geological cross-section. Inset: schematic stratigraphic section of the Cambrian-Ordovician succession of the St. Lawrence Platform in southern Quebec with, circled, the Upper Ordovician fine-grained clastic forming the

shallow bedrock of the study area (modified from Lavoie et al. 2016). Not to scale. RJC: Rivière Jacques-Cartier fault, CFS: Chambly-Fortierville syncline, Mtl: Montreal, Qc: Quebec City.

The detailed organic geochemistry of the shallow bedrock units of the study area has shown that the shale-dominated successions have some good (Lotbinière and Les Fonds formations) to low (Nicolet Formation) organic matter content and have generated and still contain volatile hydrocarbons (Lavoie et al. 2016). The isotopic ($\delta^{13}C$ and $\delta^{2}H$) compositionof methane, ethane and propane extracted from the rock indicate a thermogenic origin with increasing microbial contribution in the upper (< 50 m) and more fractured intervals of the studied cores (Lavoie et al. 2016).

Surficial sediments in this region are usually thin (< 10 m) and made up of reworked tills and near-shore sediments of the former Champlain Sea, except in a few areas where fine-grained marine sediments have accumulated in local lows of the paleo-topography. When thicker, these sediments usually contain coarser horizons that can be used for water supply, as is the case for the municipality of Saint-Édouard.

3.2 Hydrogeological context and methane in groundwater

Groundwater in the St. Lawrence Lowlands has been known to contain high concentrations of dissolved methane in certain areas since the 1950’s (Clark 1955). The Saint-Édouard region was found to contain methane in groundwater almost everywhere during our research project(Bordeleau et al. 2015, with measured dissolved methane concentrations sometimes being above saturation under atmospheric conditions. Residential wells in this area are mostly open boreholes completed into bedrock (shale) with generally unsealed metal casing across surficial sediments. Residential wells have depths that generally vary between 20 m and 80 m, with an average of about 50 m. This shale has a poor permeability, having hydraulic conductivities between 10^{-9} to 10^{-6} m/s, and the active groundwater flow zone is shallow (< 30 m within bedrock) (Ladevèze et al. 2016).

Methane concentrations in groundwater in the Saint-Édouard region is strongly correlated to the water type, with higher concentrations (up to 80 mg/L) found in water containing more sodium ($NaHCO_3$ and NaCl types) compared to relatively less geochemically evolved $CaHCO_3$ water (Bordeleau et al. 2015). These findings are in agreement with many other studies elsewhere (e.g. Molofsky et al. 2013 and 2016a; Darrah et al. 2014; LeDoux et al. 2016; Siegel et al. 2016), as well as over the entire St. Lawrence Lowlands (Moritz et al. 2015). Dissolved methane in the Saint-Édouard area was found to be of predominantly microbial origin, with contribution of thermogenic methane in approximately 15% of the wells (Bordeleau et al. 2017), which is also in agreement with the regional study over the St. Lawrence Lowlands that found predominantly microbial methane in groundwater (Moritz et al. 2015). In the study area, both types of methane were shown to come from the shallow bedrock, which is mainly composed of organic-rich shales (Lavoie et al. 2016).

There is currently no Canadian drinking water quality guideline for dissolved methane as this component is not related to a health issues. However, the Ontario drinking water standards provide an aesthetic objective for methane of 3 L/m^3 (i.e., 2 mg/L) to limit problems with gas bubble release and spurting from taps (Kennedy and Drage 2015), while the alert threshold for the province of Quebec and Pennsylvania State is 7 mg/L and for Ohio State 10 mg/L, mainly to avoid risk of explosion. The U.S. Department of the Interior recommends periodic monitoring when dissolved methane concentrations range between 10 and 28 mg/L and remedial action when concentration exceeds 28 mg/L (U.S. Department of the Interior 2001).

3 Methodology

3.1 Drilling and selection of wells for the monitoring program

Fifteen observation wells were drilled into bedrock within the framework of the project, of which eight were diamond-drilled in order to have core samples for various analyses (e.g. Lavoie et al. 2016) and five were selected for frequent groundwater monitoring. The locations of the 15 observation wells were chosen in order to achieve good spatial coverage, obtain samples from the different geological formations, and collect a higher density of data close to the faulted zones that could represent fluid migration pathways between the deep and shallow domains. Indeed, a natural connection between deep units and surficial aquifers is presumed possible only if permeable discontinuities are present, such as permeable fault zones (Gassiat et al., 2013; Birdsell et al., 2015). Therefore, most of the monitoring wells were drilled close to two known fault zones: the Logan’s Line – Aston fault system (thrust faulting) in the southern part of the study area and the Jacques-Cartier River fault (normal faulting) in the northern part (Fig. 1).

The seven (7) wells used for the temporal methane monitoring program reported in this paper were selected based both on their spatial coverage and on their range of concentrations and isotopic signatures. They included five (5) observation wells (F1, F2, F3, F4 that were diamond-drilled in 2013 and F21 that was diamond-drilled in 2014), and two residential wells (INRS-447 and Zone 9R) (Fig. 1). All the observation wells are open to the fractured rock aquifer and a sealed metal casing was put across surficial sediments and anchored in the top part of bedrock. They were developed just after completion using compressed air to empty them to make sure that the water used as a drilling fluid was removed before sampling. These observation wells are either under confined (wells F1, F3 and F4) or semi-confined (wells F2 and F21) conditions (Ladevèze et al. 2016) and their general characteristics are summarized in Table 1. The confinement of the fractured rock aquifer can either come from low-permeability surficial deposits or a lack of fractures in the upper part of the shale unit making up the rock aquifer. More details on these wells and their construction are provided in Ladevèze et al. (2016).

The use of residential wells in baseline studies has been discouraged by Jackson and Heagle (2016), mainly due to potential surface contamination by septic tank effluent, de-icing salt and agricultural residues, poor maintenance of the well and of the plumbing, as well as a poor construction. However, we wanted to include both observation and residential wells in the monitoring program, as their characteristics are very distinct: residential wells are used continuously for domestic purposes and their construction dates back several years, while our recent monitoring wells are dedicated, mostly isolated wells only pumped sporadically and at a very low yield.

Table 1 Characteristics of the monitoring wells used in this study

Site	Well type	Drilling type	Drilling year	Total drilled depth (m bgs)	Static water level (m bgs)	Overburden thickness (m bgs)	Sampling depth (m bgs)	Geological unit
F1	OW	D-D	2013	50	-0.02	2.44	7.5	Lotbinière
F2	OW	D-D	2013	52	1.55	6.1	21.5	Les Fonds
F3	OW	D-D	2013	50	0.79	20.12	22.7	Nicolet
F4	OW	D-D	2013	60	7.51	40.84	54	Les Fonds
F21	OW	D-D	2014	147	4.77	4.57	145	Les Fonds
INRS-447	RW	H-D	2009	12.8	1.22	9.2	At the tap	Lotbinière
Zone 9R	RW	H-D	1967	45.7	1.22*	5.5	At the tap	Nicolet

OW: Observation well drilled for the project; RW: Residential well used for water supply; D-D: Diamond-drilled well with a 100 mm (4 in.) diameter; H-D: hammer-drilled well with a 152 mm (6 in.) diameter; m bgs: meters below ground surface. * The only data available dates back to its drilling year (1967), as we did not get the owner authorisation to open the well.

This decision to include residential wells was also based on the fact that sampling residential (or irrigation) wells in a baseline study is almost inevitable, as it allows for a much better coverage of a study area at a reasonable cost, compared to the drilling of costly dedicated observation wells. In fact, this is typically what is done by oil and gas companies to establish baseline conditions. We therefore wanted to follow both types of wells and verify whether methane variations would be similar. While it is true that residential wells are vulnerable to the potential issues discussed in Jackson and Heagle (2016), the water geochemistry from the two residential wells selected for the temporal monitoring program has been carefully examined, to ensure these wells were suitable for monitoring and that their results were representative of natural groundwater. These two residential wells are likely under confined or semi-confined conditions like the other wells in this study area and did not appear to be contaminated by de-icing salts or other anthropogenic sources based on their general geochemistry results. Another issue with residential wells is that their usage could result in a significant drawdown in the well and, therefore, degassing in the well. The two selected residential wells were always sampled at a low flow rate during the day, while the owners were not home.

3.2 Monitoring program

Temporal geochemical monitoring began in November 2013 with the first four wells drilled for the project (F1 to F4; Table 1). The two residential wells (INRS-447 and Zone 9R), which were first sampled in summer 2013, were added to the monitoring program the next spring. The deepest observation well (F21; Table 1) was added to the program after its completion in November 2014. These wells were sampled regularly (every 2 to 3 months), except during winter, when the frequency was lower due to accessibility and freezing (when water level is close to the surface) issues such as for well F1. In the last year of the project (March 2015 - February 2016), the sampling frequency was increased to once a month for wells F4 and F1 (except in winter months for F1).

As part of the monitoring program, the collected water samples were analyzed for alkane (methane, ethane, propane) concentrations and for methane isotopic composition ($\delta^{13}C$-

CH_4, δ^2H- CH_4) when concentrations allowed (generally in the order of 150 µg/L of methane). Relatively early in the monitoring program, dissolved inorganic carbon (DIC) concentrations and its isotopic composition ($\delta^{13}C$-DIC) were also added, as these parameters could provide important information regarding the origin of methane. To our knowledge, this is the first documented record of such complete yearly geochemical time-series.

Groundwater levels were also monitored every 15 minutes in each monitoring well with pressure loggers, completed by barometric pressure measurements in three wells (F1, F2 and F4) (Ladevèze et al. 2016).

3.3 Groundwater sampling, storage and chemical analysis

Observation wells F1 to F4 were sampled using either a Redi-Flo2 impeller pump (Grundfos, Bjerringbro, Denmark) or a Solinst (Georgetown, ON, Canada) model 407 bladder pump, both with 6.25 mm (¼”) diameter tubing. Observation well F21, due to its greater sampling depth (145 m), had to be sampled using HydraSleeve (Las Cruces, NM, USA) single-use sampling bags, a simple device consisting of a polyethylene bag sealed at the bottom and with a self-sealing check valve at the top. Careful comparison of these different devices will be documented in an upcoming paper; results showed that they produce comparable results for concentrations and isotopic ratios.

Samples were always collected for a given well at the same depth (see Table 1). Packers were not used to isolate a specific interval, because this technique would have been extremely time consuming, and sampling five wells at such high frequency in this manner would not have been practically feasible. Instead, the pump or bag was slowly and carefully lowered in the well and was positioned at the depth where the most productive fracture(s) had previously been identified by borehole geophysical methods (Crow and Ladeveze 2015), to ensure that only "fresh" groundwater from the flowing fractures was being pumped. Physico-chemical profiles were carried out in four wells at 5-m intervals and the distinct characteristics obtained at each interval confirmed that the sampling method was appropriate for targeting water from a given depth. When pumps were used, the pumping rate was kept at a minimum (well below the 500 mL/min low-yield recommended by the EPA), which limited drawdown, thus preventing degassing of the water in the well. The median drawdown was 59 cm for monitoring wells F1 to F4, due to the very low-permeability rock. The two residential wells (INRS-447 and Zone 9R) were sampled upstream from any treatment system, using 6.25 mm (¼") diameter tubing connected to the outdoor spout. Sampling was again performed at a very low yield (below the recommended 500 mL/min) to minimize drawdown (average yield was 260 mL/min). It was carried out during the day when the wells had not been used for a few hours. While the use of an outdoor tap when the owners were not home can result in some gas loss (although all sampled water tanks were pressurized), this also ensures that no domestic device uses water at the time of sampling, which could cause important drawdown in the well.

For all wells, samples for alkane concentrations and isotopic composition were collected by placing the sampling bottle (40 mL glass amber vials for concentrations and 1L amber glass bottles for isotopes) in a larger container, and positioning the sampling tube at the bottom of the bottle, as recommended for analyses of dissolved gas by the U.S. Geological Survey (http://water.usgs.gov/lab/chlorofluorocarbons/sampling/bottles/). Water filled the bottle, then the larger container. The tube was slowly removed from the submerged bottle, and the bottle was rapidly capped under water. This sampling procedure represents a "semi-closed" system, as described by Molofsky et al. (2016b). Such a sytem provides good results for low and intermediate methane concentrations (i.e. samples not supersaturated with dissolved gases), but methane concentrations in gas-charged (effervescing) samples are likely underestimated (Molofsky et al., 2016b). However, obtaining exact concentrations was not crucial for this study, because the monitoring program was mainly put in place to follow stable isotope ratios so as to identify methane origin. Nonetheless, documenting the extent of methane concentration variations obtained under these typical sampling conditions was also deemed valuable. The pH in the samples was lowered to <2 using hydrochloric acid to prevent microbial activity, and the bottles were kept refrigerated either upside down or on their side. Samples for δ^{13}C-DIC were collected by simply filling the 40 mL amber glass vials completely (without air) with filtered groundwater (using a 0.45 µm nylon membrane). These samples were not acidified, as this would have caused degassing of CO_2.

Concentrations of alkanes were determined at the Delta-Lab of the Geological Survey of Canada (Quebec City, QC, Canada) using a Stratum PTC (Teledyne Tekmar, Mason, OH, USA) purge and trap concentrator system interfaced with an Agilent (Santa Clara, CA, USA) 7890 gas chromatograph equipped with a flame ionisation detector (GC-FID). Quantification limits on the samples were 0.006, 0.002, and 0.01 mg/L for methane, ethane and propane, respectively. Methane carbon and hydrogen stable isotope ratios were analyzed at the Delta-Lab, at the G.G. Hatch laboratory of the University of Ottawa (ON, Canada) or at Concordia University (Montreal, QC, Canada) using gas chromatographs interfaced with isotope ratio mass spectrometers (GC-IRMS). The methane in some samples was analyzed in duplicate at the three labs to ensure that results were comparable. Details concerning the analytical procedures and quality control at each lab are found in Appendix A5. Results are expressed in the usual per mil notation relative to Vienna Pee Dee Belemnite (VPDB, for $\delta^{13}C$) and Vienna Standard Mean Ocean Water (VSMOW, for $\delta^{2}H$). Precision is typically $\leq 0.5‰$ for $\delta^{13}C$ and $\leq 3.0‰$ for $\delta^{2}H$. Finally, analyses for $\delta^{13}C$-DIC were done at the University of Waterloo (ON, Canada) using a MicroGas-IsoPrime (Manchester, UK) mass spectrometer, and results are expressed with respect to VPDB. Precision is ± 0.2‰.

3.4 Estimation of uncertainty related to sampling, handling and analytical procedures

The uncertainty due to sampling, handling and analytical procedures was evaluated for alkane concentrations and methane C and H isotopes, using replicate samples collected within the framework of the larger Saint-Édouard project. For concentrations, 55 samples were collected and analyzed in triplicate. For each sample, the three bottles were collected within a few seconds of one another in the field, under the same conditions and in the same larger container, and were analyzed (one analysis each) sequentially. Methane concentrations in the 165 bottles (55 samples x 3 bottles) varied between 0.15 and 57.2 mg/L. For convenience of comparison with other papers, the uncertainty was assessed through two common approaches, i.e. using either the relative error ($[C_{max}-C_{min}]/C_{max}$) or the coefficient of variation (CV= standard deviation / mean). Relative errors and CVs were used to remove the dependence of uncertainty on absolute concentrations. Indeed, methane concentrations in our samples vary over nearly three orders of magnitude, and so does the absolute uncertainty; hence, the use of relative values provides one criteria that is applicable to all samples. For both approaches, descriptive statistics are presented in Table A1 in Appendix A2. This table includes the minimum, maximum, median, and 90th percentile values, all expressed in percent (%). Although estimated with only three values each time, CVs provide an order of magnitude of the uncertainty that is useful for later comparaison with monitored concentrations (in section 4). The statistics selected to represent the uncertainty on all the methane concentration values in this research project is the 90th percentile value of the coefficient of variation and is 15% in this case.

The approach used to estimate uncertainty on isotope ratios was slightly different, mainly due to the higher analytical costs, and to the larger volume of water that needs to be collected, handled and stored (3 x 40 mL bottle for concentrations versus 2 x 1L bottle for isotope ratios). For the isotope ratios, an absolute uncertainty value may be reasonably estimated, because the variations in magnitude between the isotopic ratios of individual samples are actually very small; hence, the uncertainty is not very much affected by individual sample results. Standard deviation is therefore used for convenience of expressing uncertainty in per mil (‰) (Table A1). For methane carbon and hydrogen stable isotope ratios, 15 samples were collected in duplicate in the field. The selected statistics for methane isotopes is the 90th percentile value of the standard deviation rounded off to the nearest integer, which is 1.7‰ for carbon isotopes ($\delta^{13}C$) and 19‰ for hydrogen isotopes ($\delta^{2}H$).

4 Results and related discussion

Results obtained for residential wells are considered separately from those for observation wells, since residential wells are used on a daily basis and could be subject to different conditions affecting the concentrations and isotopic composition of methane (see Section 3.1). All geochemical results will be available in a public database to be released in 2017, excluding name and address of well owners, as well as the geographical coordinates of residential wells.

4.1 Concentrations of methane and higher alkanes

Concentrations measured in the selected monitoring wells are representative of the region, and temporal variations of these concentrations are shown in Figures 2 and 3. For the two residential wells, methane concentrations data go from summer 2013 to winter 2016, whereas values for the observation wells either begin in the fall of 2013 (F1 to F4) or 2014 (F21) depending on their completion date. Values for methane concentrations were classified either as “low” (detection limit to 1 mg/L), “intermediate” (1 to 7 mg/L, the latter corresponding to the alert threshold for the Quebec Department of Environment), or “high” (> 7 mg/L).

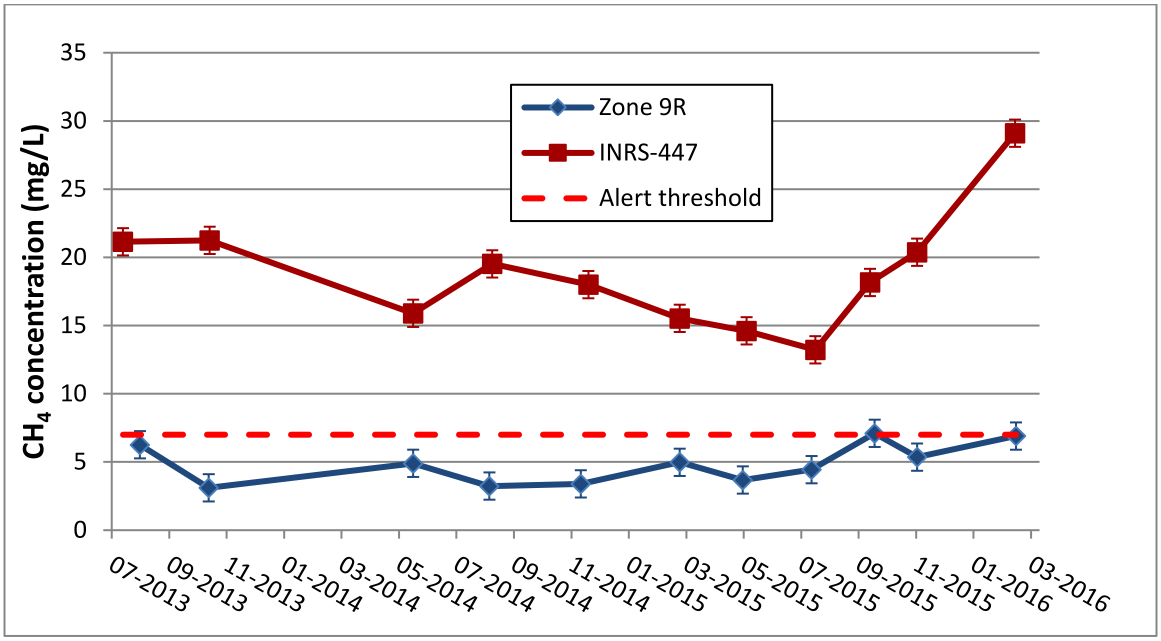

Fig. 2 Methane concentrations over time for the two residential wells. Uncertainty, represented by error bars, is ±15% of the values. The alert threshold for the Department of Environment of Quebec (7 mg/L) is shown using a dashed red line. Note: These two wells were sampled the first two times using a 19 mm (¾’’) garden hose, then using a 6.25 mm (¼’’) hose, which may have led to an underestimation for well INRS-447 as concentrations are high.

Water from both residential wells is of the geochemically evolved $Na-HCO_3$ type and contains hydrogen sulfide, with the accompanying typical strong “rotten egg” odor. Well Zone 9R, constructed in 1967, is located along the Jacques-Cartier River fault in an area underlain by the organic-lean Nicolet Formation (Lavoie et al. 2016) (Table 1 and Fig. 1).

Well Zone 9R exhibits “intermediate” methane concentrations, varying between 3.1 and 7.1 mg/L, with a CV of 52% and a maximum over minimum (max/min) concentration ratio of 2.29. Noteworthy, while ethane has never been detected in samples from this well, propane was present in the first sample (350 μg/L), but was never detected in subsequent samples. One factor that differs between the first sampling event and the following ones is the duration of pumping before sampling, which was much longer at the first visit (about 90 minutes compared to 20 minutes for the subsequent visits). This well is not very productive and, due to water shortage resulting from our first visit, the owner required that we pump for a shorter period of time in the future. However, as this well is regularly used for domestic needs, the physico-chemical parameters have always reached stability within this 20-min period. It is inferred that the longer pumping time during the first sampling event had drawn in water from different, lower strata, where thermogenic gas (containing propane) is present.

Well INRS-447, constructed in 2009, is located within a few tens of meters of the St. Lawrence River in an area underlain by the Lotbinière Formation, which is hydrocarbon volatiles-rich (Lavoie et al. 2016) (Table 1 and Fig. 1). In residential well INRS-447, methane concentrations are high and variations in the absolute concentrations are greater than for the previous well, with observed measured concentrations between 13.2 and 29.1 mg/L. However, the relative variation is lower, with a CV of 25% and a max/min concentration ratio of 2.20. Methane concentrations in this well gradually decreased during the first 2 years (from 21 mg/L to 13 mg/L). Nonetheless, a marked increase is observed in the last three sampling campaigns (Fig. 2), similarly to most observation wells (see below). Groundwater consistently contained ethane and propane, with median concentrations of 96 and 78 μg/L, respectively. In all but one sample from this well, the proportions of methane to ethane + propane (dryness ratio) varied between 103 and 656, pointing towards mixed thermogenic and microbial gas origin (results of dryness ratios over time are provided in section A3 of the Appendix).

Observation wells F1, F2, F4 and F21 have “high” (>7 mg/l) methane concentrations, while well F3 generally has “low” (detection limit to 1 mg/l) concentrations. As for the residential wells, high concentrations are found in wells drilled in the hydrocarbon volatiles-rich Lotbinière and Les Fonds formations (i.e. wells F1, F2, F4 and F21, see Table 1 and Fig. 1). For all wells, concentrations vary considerably over time, with CV of 34% for F1, 57% for F2, 236% for F3 (although large in percentage due to the first higher value, absolute changes in concentration were not major for this low concentration well; see Figure 3), 22% for F4 (54 m depth), and 45% for F21. The temporal variation in each well is therefore higher than the combined uncertainty introduced by sampling, handling and analytical procedures, which is 15% (see section 3.4).

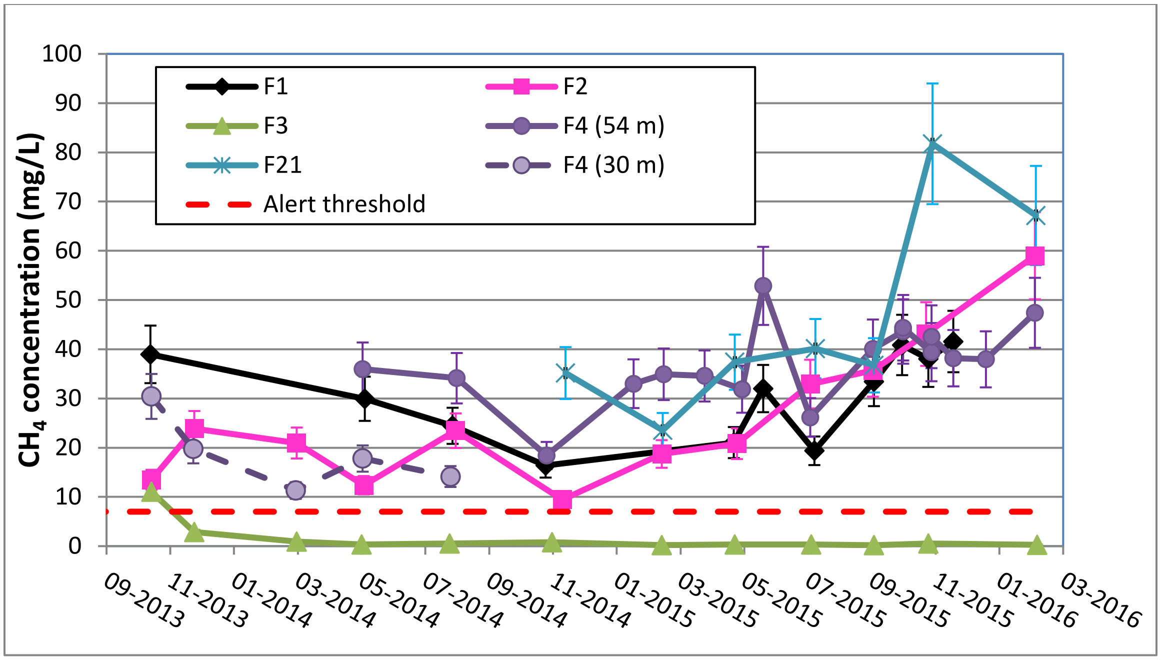

Fig. 3 Dissolved methane concentrations over time for the five observation wells. Uncertainty, represented by error bars, is ±15% of the values. Notes: 1) the first two values for wells F2, F3 and F4 were obtained using an impeller (Redi-Flo2) pump that had a 19 mm (3/4’’) tubing, which may have lead to more degassing and thus underestimated methane concentrations; 2) well F4 was initially pumped at a depth of 30 m, before a 90-m impeller pump was available.

For well F3 (drilled in the Nicolet Formation), the first value obtained a few days after drilling was 11 mg/L. Concentrations rapidly dropped in the following months and have remained between 0.1 and 1 mg/L for the last two years. This is likely due to the fact that some of the methane contained in the rock surrounding the borehole was rapidly released during and after drilling, while the free-flowing groundwater contains very little methane.

A somewhat similar situation occurred at well F1 (in the Lotbinière Formation), which was visibly degassing just after drilling, with audible bubbling and fumes coming out of the well, which stopped a few weeks later. In this well, methane, ethane and propane concentrations were highest a few weeks after drilling (39.0, 4.8 and 3.4 mg/L, respectively) and then declined during the first year. However, methane concentrations started to rise the second year to eventually reach values similar to the one obtained during the first sampling campaign, but this was not the case with ethane and propane. It is therefore likely that the thermogenic gas present in the rock was released shortly after drilling, being then replaced by mixed gas (with a higher proportion of microbial gas) found in groundwater. The dryness ratio of 10 obtained in the first sample was the lowest of the series, but the subsequent ratios remained quite low (between 44 and 247), within the thermogenic or mixed gas domains (see Appendix A3). Only two samples from F1 had no detectable ethane or propane, indicating a strong predominance of microbial gas at that time (confirmed by isotopic ratios, see below).

For well F4 (in the Les Fonds Formation), the first value of five obtained at the 30 m depth was also the highest concentration recorded at this depth. The same early degassing situation as for F1 and F3 is thus suspected, although it is difficult to draw a firm conclusion since the following concentrations were obtained at greater depth (Fig. 3). The concentration at a 30 m depth appears to be approximately half of that at 54 m based on the two sets of samples taken the same day, confirming that sampling must always be done at the same depth within a timeseries in order to have comparable data.

In wells F2 and F21 (also in the Les Fonds Formation), early degassing is not suspected, as the concentrations in the first samples are not the highest of the series. Well F2 contains microbial gas (based on the very low ethane and propane concentrations, and on isotopic ratios of methane, see below), while well F21 consistently contained ethane and propane, with dryness ratios varying between 27 and 46, indicating the presence of thermogenic gas.

In four of the five observation wells, the max/min methane concentration ratios are somewhat similar (2.54 for F1, 6.26 for F2, 2.87 for F4, 3.47 for F21), and resemble the ratios in residential wells. In contrast, the max/min ratio is much higher for well F3 (>58), because the first two values (and especially the first one) from this well were much higher than the subsequent ones (this ratio drops to 5.2 when rejecting the first two values). In most of our monitoring wells (except F3 and Zone 9R), an increase in methane concentration was observed during the second year of sampling. In observation wells, the increase generally began in November 2014, while the rise for the residential well INRS-447 started only in July 2015. Because the project ended in March 2016, we do not know whether the concentrations would have continued to increase, thus increasing the max/min ratios.

Ethane concentrations were above a few µg/L only in three wells (INRS-447, F1 and F21; all in the volatiles-rich Lotbinière and Les Fonds formations); they showed a quite good coefficient of correlation with methane concentrations (R^2=0.77). Propane in groundwater was present in significant concentrations over time only in well F21, and the seven data available showed a weak coefficient of correlation with methane (R^2=0.30). Dryness ratio values over time for the 7 observation wells are presented in Appendix (section A3). They also show highly variable values, except for well F21 that has relatively stable ratios mainly due to the quite good correlation between methane and ethane concentrations.

In an attempt to explain the temporal variation for methane concentrations in the different wells, total precipitation and water level (corrected for barometric pressure changes) time-series were plotted against available methane concentrations. Comparisons were made using daily, weekly and monthly precipitation and water-level data (not shown). Methane concentrations do not appear to be strongly related to precipitation or groundwater levels, either seasonally or over the whole period. Methane concentrations in a well (and even more so in a collected water sample) depend on multiple factors, and recharge is a complex process resulting from all the other water budget components. Hence, it does not appear possible for methane concentrations to be predicted using parameters such as precipitation and water levels, at least in the study area. It is expected that other regions that share a similar hydrogeological context with high concentrations of dissolved methane in shallow low-permeability aquifer would behave similarly (e.g., in Pennsylvania and West Virginia as described in Sharma et al. 2013, Molofsky et al. 2013; Siegel et al. 2015).

4.2 Methane isotopic composition

The main interest of this study was to investigate whether methane carbon and hydrogen stable isotope ratios varied over time, as do methane concentrations (Figures 4 and 5). In most samples, carbon stable isotope ratios ($\delta^{13}C\text{-}CH_4$) are between -70 and -50‰, and are therefore somewhat close to the boundary between the typical isotopic domains defined for thermogenic gas (> -50‰) and microbial gas (usually < -60‰, but sometimes heavier, i.e. between -50 and -60‰, when originating from acetate fermentation or when subjected to post-genetic transformation processes), as suggested by several authors (e.g. Whiticar 1999; Golding et al. 2013). Such intermediate values can be the result of mixing between gas of different origins, or alterations of microbial gas through processes that increase the $\delta^{13}C$ value, such as partial methane oxidation or methane generation from an old, partially exhausted carbon reservoir (late-stage methanogenesis) (Bordeleau et al. 2015). An in-depth study of the origin of the methane found in the different wells of the study area will be the subject of an upcoming paper.

Figure 4 shows that residential well INRS-447, which has high methane concentrations (Fig. 2), exhibits $\delta^{13}C$ values steadily around -60‰, with a standard deviation (SD) of 1.5‰. Its variations throughout the timeseries are therefore within the variations expected from sampling, handling and analysis (1.7‰ for SD see Table A). As mentioned in section 4.1, samples from this well consistently contained ethane and propane, with resulting dryness ratios being in the mixed thermogenic/microbial domain (see Figure A1 in Appendix A3). In this case, mixing between both sources appears to be rather uniform in parts of the aquifer penetrated by the well, which results in relatively constant $\delta^{13}C$ values obtained in the timeseries.

In contrast, in residential well Zone 9R, which contains intermediate methane concentrations, the first sample has a significantly higher $\delta^{13}C$ ratio (-43.5‰) compared to subsequent samples (Fig. 4a); it was also the only sample from this well to contain propane. All subsequent $\delta^{13}C$ values obtained from this well were within the microbial domain (-61.3 to -76.6‰), but varied more than in well INRS-447 (SD of 8.0‰ when including the first sample, and SD of 4.0‰ when excluding it). The variations in the timeseries therefore exceed the uncertainty related to sampling, handling and analysis. The isotopic values in well Zone 9R support our earlier hypothesis that the longer pumping time and higher pumping rate exerted during the first sampling event drew in water from different strata containing thermogenic gas. Therefore for this well, it seems possible to obtain gas from different origins, but the proportions are not stable and rather depend on pumping duration and the related drawdown.

In observation wells F1, F2, F4 (30 m and 54 m) and F21, variations of $\delta^{13}C$ are also limited (Fig. 4b), with SDs ≤ 2.2‰. Variations are therefore somewhat comparable to residential well INRS-447, and generally lie within the uncertainty expected for sampling, handling and analysis. In well F3, lower $\delta^{13}C$values (-95 to -63‰) compared to those of the other wells were found, and variations are much more important, with a SD of 10.8‰. In this well, ethane and propane were never detected, but this may only be due to the fact that methane concentrations are very low (generally below 1 mg/L), so a mixed gas origin cannot be excluded. However, even if the gas is entirely microbial, due to the low methane concentrations, processes affecting the methane (e.g. oxidation), even if occurring to a limited extent, could have a pronounced effect on the isotopic ratios (see below).

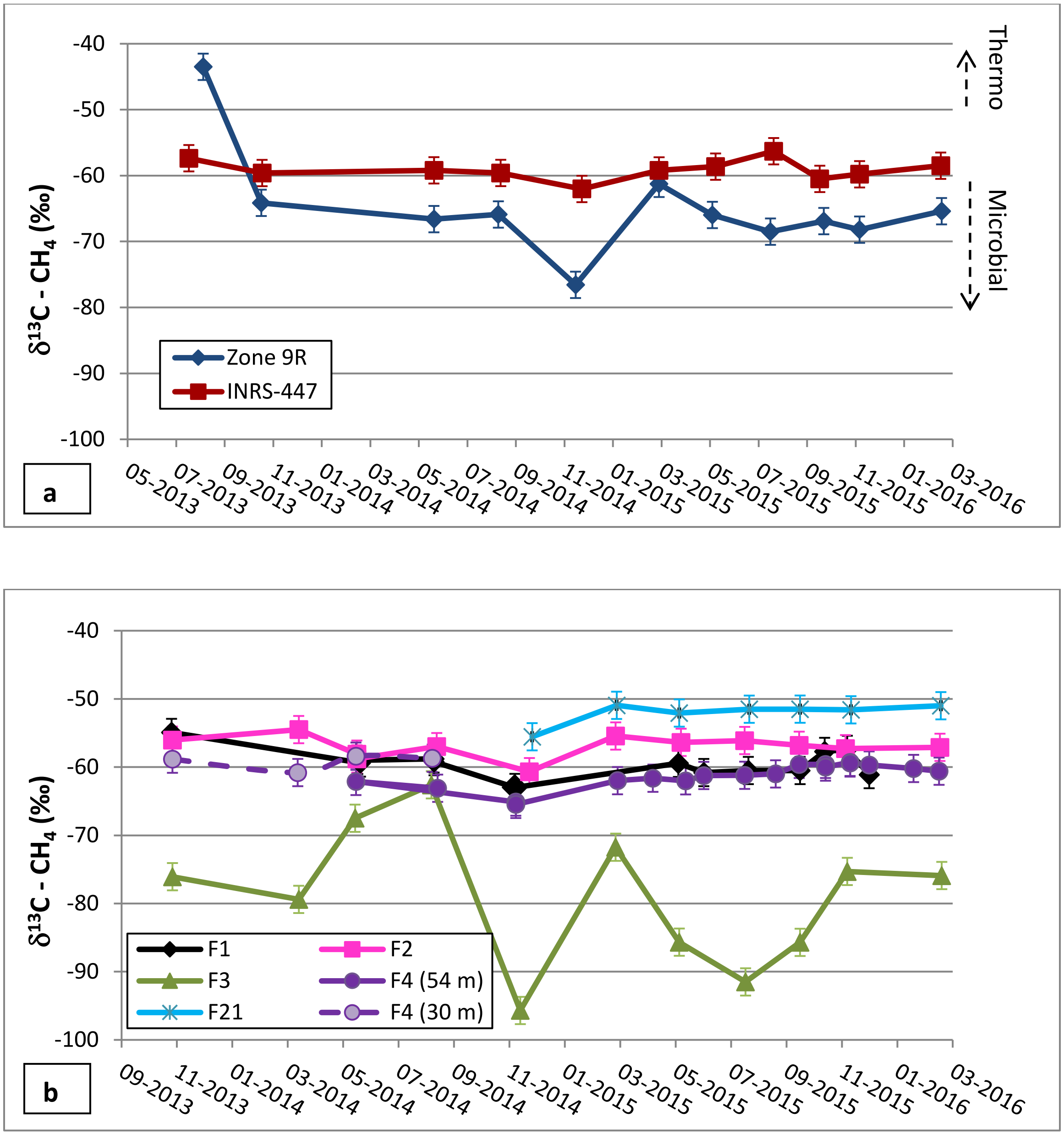

Fig. 4 Carbon isotopic ratios ($\delta^{13}C$-CH_4) over time for the two residential wells (a) and the five observation wells (b). Uncertainty, represented by error bars, is ±1.7‰. Note: Thermo: thermogenic.

Hydrogen stable isotopic values (δ^2H) were also monitored over time. These values are normally more variable than $\delta^{13}C$ (Whiticar 1999; Golding et al. 2013) and there is considerable overlap between the hydrogen isotopic domains defined for microbial and thermogenic gas. The δ^2H values must always be used together with $\delta^{13}C$ values in order to provide useful information concerning the origin of methane, because methane of thermogenic and microbial origins would not necessarily have distinct δ^2H values. However, if processes such as oxidation affected methane in groundwater, the isotopic effect would be more pronounced on hydrogen isotopes than on carbon isotopes (Alperin et al. 1988; Grossman et al. 2002; Kinnaman et al. 2007).

In most of the wells, δ^2H values were remarkably stable over time (Fig. 5). In residential wells, the SDs are 7.7‰ for Zone 9R (excluding the first sample of the series, as there was no δ^2H value available for this sample) and 9.6‰ for INRS-447. Similar results were obtained for observation wells F1, F2, F4 (54 m) and F21, with SDs ≤ 11.5‰. An exception is well F4 (30 m depth), which had a surprisingly high δ^2H value of -157‰ in the first sample. No explanation has been found for this first value, as there does not seem to be a mixing between microbial and thermogenic gas sources (no ethane or propane were detected) and oxidation does not seem plausible (the carbon isotopic ratio in the first sample is not different from subsequent samples).

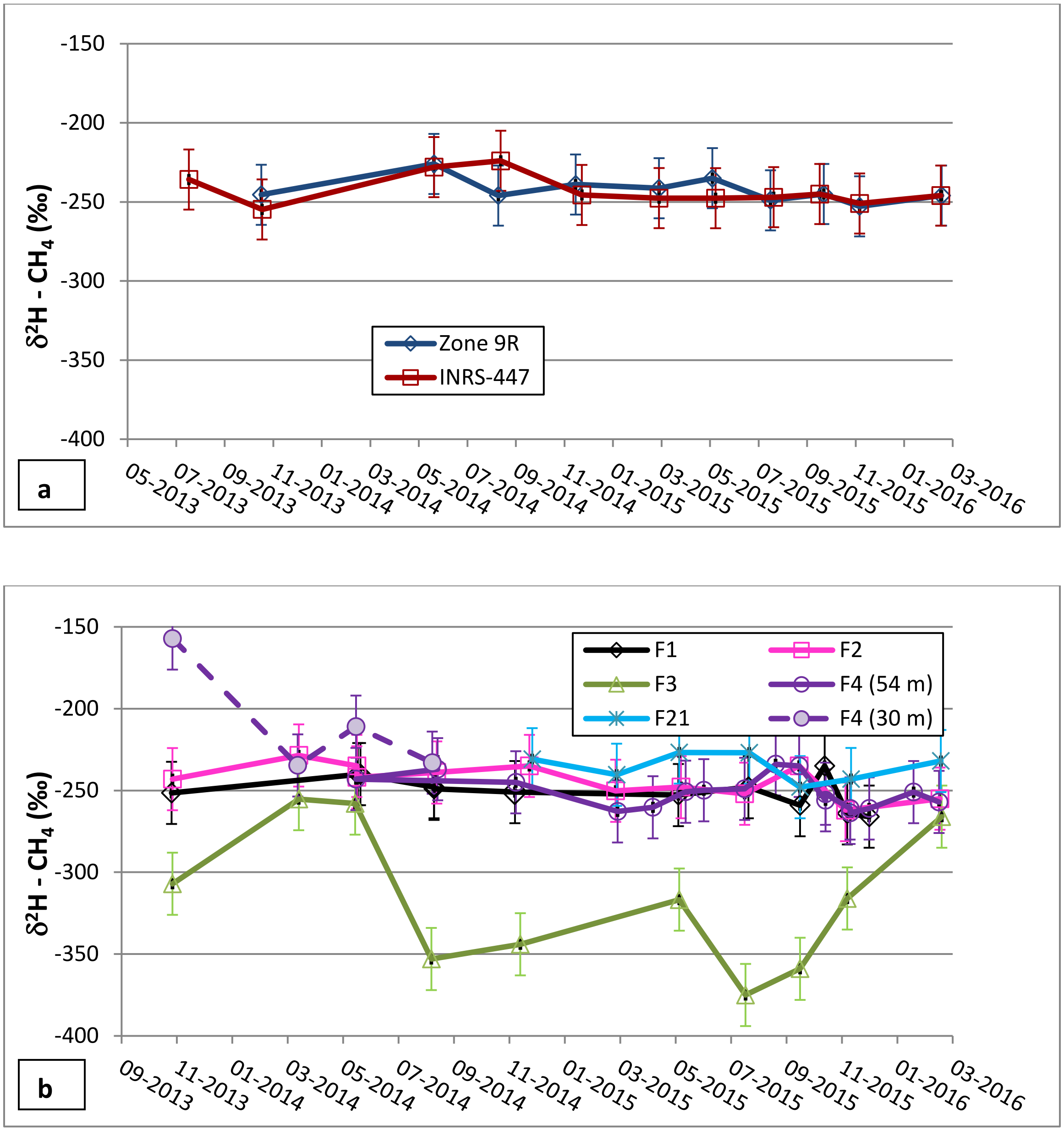

Fig. 5 Values of methane hydrogen isotope (δ^2H-CH$_4$) over time for the two residential wells (a) and the five monitoring wells (b). Uncertainty, represented by error bars, is ±19‰.

In well F3, as for $\delta^{13}C$ values, the $\delta^{2}H$ values are lower (between -375 and -255‰) and more variable than in the other wells, spanning an impressive range of 120‰, with a SD of 46.1‰. This suggests that methane may have been partially oxidized in this well and because concentrations are low, the isotopic effect is readily perceptible. To evaluate this hypothesis, we considered fractionation factors (α) documented by various authors (Alperin et al. 1988 and authors therein; Kinnaman et al. 2007; Grossman et al. 2002), which vary between 1.005 and 1.031 for carbon, and between 1.103 and 1.325 for hydrogen. An original (non-oxidized) isotopic ratio of -95‰ was selected for carbon and of -400‰ for hydrogen, based on the results of one of the F3 samples obtained with HydraSleeve bags (thus not shown in Figures 4 and 5): $\delta^{13}C$ = -95‰ and $\delta^{2}H$=-393‰ for a methane concentration of 0.48 mg/L. These values, although extremely low, are nonetheless within the range of uncertainty of the loest values shown in Figure 5b. The range of $\delta^{13}C$ versus $\delta^{2}H$ values that could result from progressive methane oxidation was calculated using the afore-mentioned fractionation factors (shown as a grey area in Fig. 6). Most of the data points from well F3 do fit within this range (see Fig. 6), in support of the oxidation hypothesis, to explain the highly variable isotopic ratios measured in this well.

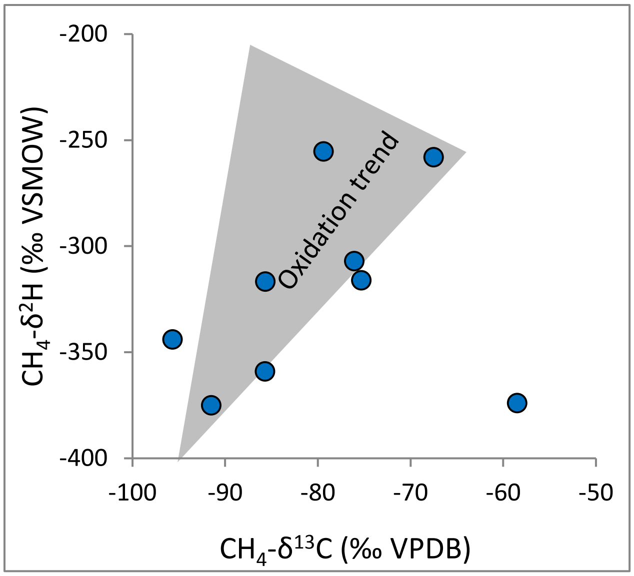

Fig. 6 Isotopic values ($\delta^{13}C$ and $\delta^{2}H$) for methane in well F3 (circles) and range of isotopic values that could result from progressive methane oxidation (grey area).

Figures 4 and 5 reveal that wells from this study area that have high methane concentrations (>7 mg/L) generally have stable carbon and hydrogen isotope ratios with variations within the expected uncertainty arising from sampling, handling and analysis. However, wells that have low or intermediate methane concentrations (such as F3 and Zone 9R) appear to have carbon and hydrogen stable isotopic values that vary more importantly over time, being influenced either by mixing of two gas sources in varying proportions or by partial methane oxidation. Because wells Zone 9R and F3 have lower methane concentrations than other wells in the monitoring program, any process affecting methane would have an impact on both stable isotope ratios that is more significant than in other wells, as long as these processes involve a change in isotopic ratios (i.e. mixing of groundwater sources that have distinct isotopic signatures or post-genetic processes that cause isotopic fractionation).

4.3 Dissolved inorganic carbon isotope ratios (δ^{13}C-DIC)

The δ^{13}C-DICvalues were also monitored over time, mainly to provide additional information on methane origin within the framework of the larger project. DIC is mainly composed of two major species: CO_2, mostly from decaying modern organic matter and HCO_3^-, predominantly deriving from carbonate rock dissolution (Sharma and Baggett 2011). The soil CO_2 derived from plant decay typically has δ^{13}C values ranging from -23 to -27‰ under temperate climates where C3 plants (most common in cool, wet climates) are dominant (Clark and Fritz 1997; Sharma et al. 2013). As CO_2-laden water percolates through the soil profile, it can dissolve carbonate minerals which typically have an original δ^{13}C value very close to 0 ± 2‰ when, as in our case, carbonates were formed in a marine environment (Sharma et al. 2013). This creates a mixing model whose boundaries should be the carbon stable isotope ratios of the two distinct DIC sources. In fact, DIC in most groundwaters circulating in Lower Paleozoic or older rocks (i.e. before the advent of terrestrial plants and associated terrestrial carbonates) is made up of similar proportions of both end members and have a δ^{13}C value ranging between -11 and -16‰ (Sharma et al. 2013). However, positive values of δ^{13}C-DIC may be encountered when microbial methanogenesis significantly affects the DIC pool in an aquifer. Indeed, due to preferential use of ^{12}C by methanogens (Sharma and Baggett 2011), the two major documented methanogenic pathways (acetate fermentation and CO_2 reduction, which are both composed of several reaction steps) progressively increase the δ^{13}C value of the associated DIC pool (Whiticar 1999; Martini et al., 2003; Sharma et al., 2013).

At the onset of methanogenesis, when the DIC pool is large compared to the amount of methane produced, isotopic effects (i.e., food preference of microbes) might not be perceptible. The same is true if methanogenesis occurs in an open groundwater system where fresh, isotopically-light DIC is being added at a sufficient rate. In contrast, an important ^{13}C–DIC enrichement will be particularly significant in old, hydraulically isolated groundwater systems where the extent of methanogenesis is important, and where the DIC pool is not being replenished by regular input of fresh, isotopically-lighter DIC (Whiticar 1999). While low δ^{13}C–DIC values do not exclude methanogenesis, values above +2 or +3‰ are a good indication of its occurrence, while values above +10‰ constitute an unequivocal indication (Sharma et al. 2013). A significant increase in δ^{13}C–DIC values in a well where such values are normally stable could indicate some replenishment from a deeper source of methane. Of note, groundwater with very high values of δ^{13}C-DIC may contain both microbial and thermogenic methane (well F21 is a good example, see below).

Figure 7a shows that residential well Zone 9R has stable and more typical δ^{13}C-DIC values for groundwater according to Sharma et al. (2013), varying between -10.5 and -13.5‰. Except for the first sample, methane from this well is solely of microbial origin, and the fact that methane does not show high δ^{13}C-DIC values simply indicates that either: 1) the carbon pool from which it is produced is being replenished by fresh carbon or 2) the carbon pool is large and methane production is comparatively limited, such that the effect of methanogenesis is not apparent on the δ^{13}C-DIC values. In fact, Zone 9R is one of the two wells with the highest concentration ratios of DIC/methane (between 17 and 28), confirming that the carbon pool is important compared to the methane production. Moreover, tritium analyses, which were conducted for the larger project, have shown that there is an important modern component in the water from this well (8.2 tritium units, or TU, see Table A2 in Appendix A4), indicating that there is likely some input of fresh carbon in the aquifer. In the first sample collected from this well, a thermogenic gas component was measured ($\delta^{13}C$-CH_4 of -43.5‰), but unfortunately no $\delta^{13}C$-DIC value is available for this sample. However, the presence of thermogenic gas in this first sample would not necessarily have altered the $\delta^{13}C$-DIC value.

The other residential well, INRS-447, consistently contained gas of a mixed thermogenic and microbial origin. It has a comparatively higher $\delta^{13}C$-DIC values compared to well Zone 9R, varying between -2.6 and +3.6‰ (Fig. 7a). This may be due to the fact that the DIC/methane ratios (between 6 and 13) are smaller than in Zone 9R and, hence, the isotopic effects of methogenesis in well INRS-447 may be more visible on the DIC pool. Moreover, the modern component of groundwater appears to be slightly less important (tritium result of 5.7 TU, see Table A2), which suggests that the input of fresh carbon might be somewhat more limited.

Among the observation wells, F3 is the only one with stable $\delta^{13}C$-DIC values that are close to theoretical values for groundwater flowing into Lower Paleozoic aquifers, varying between -9 and -11‰ (Fig. 7b). Methane concentrations in this well are low and the DIC/methane ratio is the highest of all monitoring wells, being between 25 and 140, except in the first sample where it was lower (5.8) due to the suspected early degassing of the surrounding rock after drilling of the borehole. The low methane concentrations in groundwater (especially compared to DIC) are not causing visible isotopic effects on the DIC pool, although the methane is probably of microbial origin.

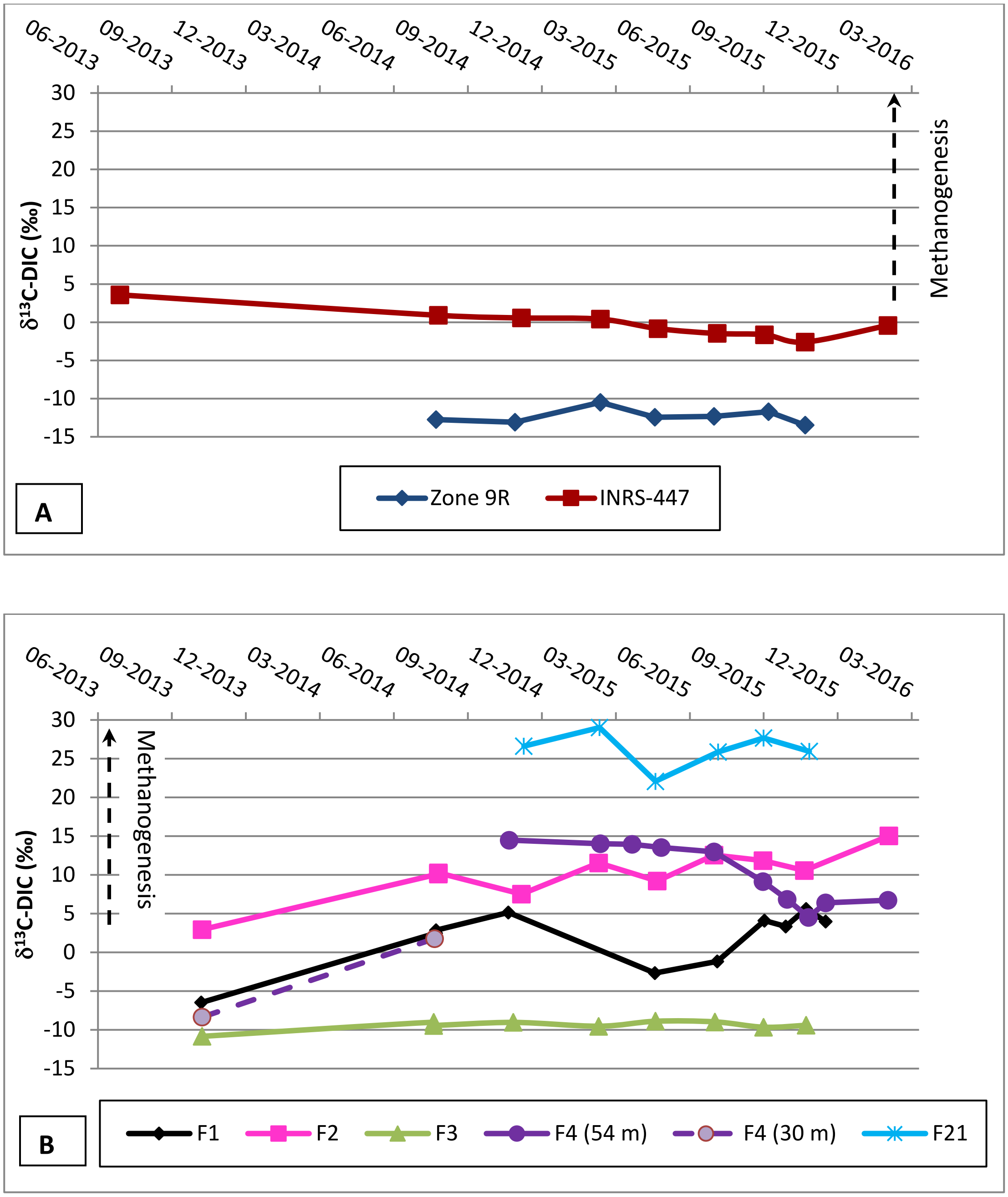

Fig. 7 Values of δ^{13}C-DIC over time for residential wells (a) and observation wells (b)

The other observation wells have higher δ^{13}C-DIC values and more pronounced variations over time (Fig. 7b). Wells F2 and F4, containing essentially microbial gas, have δ^{13}C-DIC values varying between +3 and +15‰, with half of the values being above +10‰, suggesting strong microbial activity. The methane concentrations in these wells are high, and DIC/methane concentration ratios are relatively low, varying between 1 and 10. Their tritium content is lower than in the residential wells, with 3.8 and 1.3 TU in F2 and F4, respectively (Table A2). This indicates that input of fresh carbon might be very limited in these wells. Hence, the important methanogenic activity combined to isolated groundwater conditions for these wells likely explains why the effect of methanogenesis is so significant on the isotopic values of the DIC pool.

In contrast, wells F1 and F21 contain a mix of thermogenic and microbial gas, either in varying (F1) or more stable (F21) proportions over time. In F1, the magnitude of variations in δ^{13}C-DIC values is similar to wells F2 and F4; however the values themselves tend to be more depleted, being between -6.5 and +5.6‰ (see Figures 7b and 8a). In this case, the variations appear to be related to the proportions of thermogenic and microbial gas in the samples, as reflected by the relationship between dryness ratio and δ^{13}C-DIC values (Fig. 8a). Samples with more microbial gas in the well F1 time-series have a higher dryness ratio (less ethane and propane), lower δ^{13}C-CH_4 ratios and higher δ^{13}C-DIC ratios.

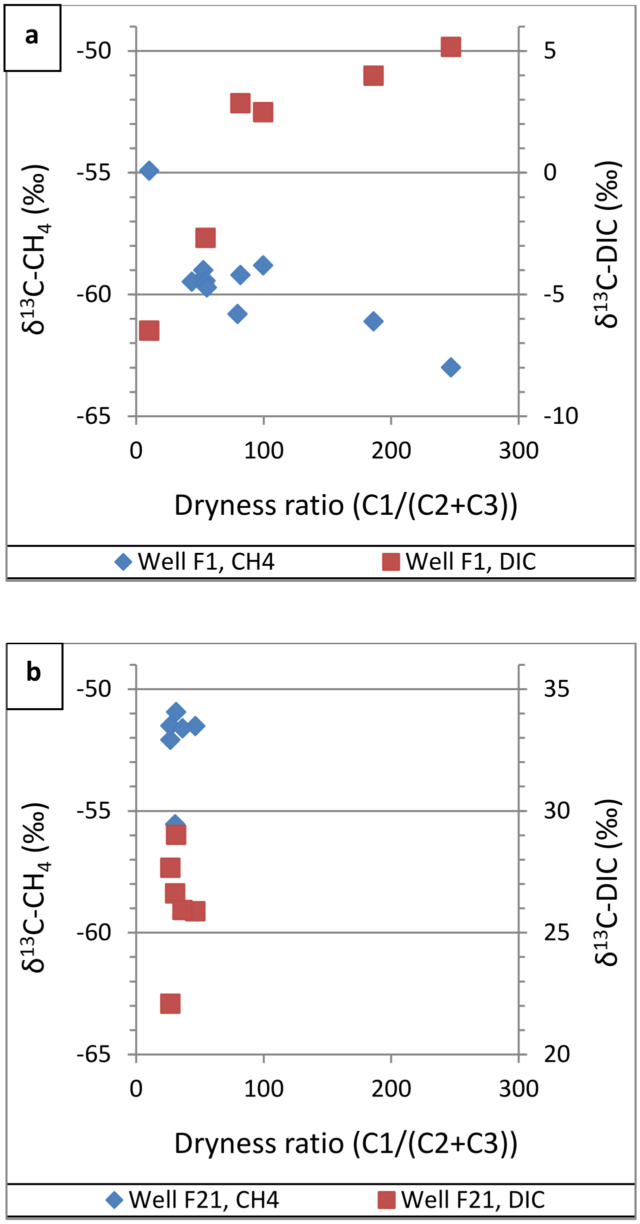

Fig. 8 Carbon isotopic values of methane (CH_4) and dissolved inorganic carbon (DIC) as a function of dryness ratio, for wells F1 (a) and F21 (b).

Such correlation is not observed for well F21, which has stable dryness ratios and fairly constant δ^{13}C-CH_4, but with more variable and overall higher δ^{13}C-DIC compared to F1

(Fig. 8b). While the proportions of thermogenic and microbial gas appears to remain relatively constant, well F21 was shown to contain a small component of relatively deep formation water (to be discussed in an upcoming publication). Based on the ion chemistry of the water, this proportion was estimated to be around 1.6%, resulting in groundwater that contains at least 5 times more TDS than in the other monitoring wells. The inflow of even a small anount of formation water from an old, isolated groundwater system located at some deeper intervals (where δ^{13}C-DIC are very high due to reservoir exhaustion) in the relatively shallow (147 m) F21 well, could explain the δ^{13}C-DIC values which reached up to +29.0‰. As a comparison, formation waters from the Antrim Shale, which is both a source and a reservoir for methane that is at the margin of the preserved depositional basin, has methane of demonstrated microbial origin with δ^{13}C-DIC values ranging from +20 to +32‰ (Martini et al., 1998). This study had underlined that these δ^{13}C-DIC values (similar to what was found in well F21) were among the highest reported values for subsurface formation waters. Well F21, in which high δ^{13}C-DIC values occur along with the presence of important concentrations of ethane and propane (up to 3.15 and 1.58 mg/L, respectively) is a good example of co-occurrence of two distinct sources of gas.

5 Further discussion and implications for future studies

In most methane baseline studies (e.g., Molofsky et al. 2013; Moritz et al. 2015; Siegel et al. 2015; 2016; Sherwood et al., 2016; Harkness et al., 2017, Nicot et al., 2017), residential wells were predominantly or exclusively used, although some authors advised against the use of residential wells due to various concerns about well and sample integrity (Jackson and Heagle 2016). In our study, the use of both residential and observation wells proved to be enlightening. Variations in methane concentrations and its carbon and hydrogen stable isotope ratios were not found to be higher with residential wells than with dedicated observation wells. We therefore consider that, when chosen carefully and properly characterized geochemically, residential wells can provide valuable information and a denser spatial coverage than what can be afforded with dedicated observation wells. As with dedicated wells, sampling at residential wells should be done at a low flow and preferably when the owners are not using water for domestic purposes at the same time, to minimize drawdown. On the other hand, observation wells drilled for the project allowed sampling water from a known targeted depth and provided a variety of highly valuable information such as geochemical results in strategic locations, change of geochemistry over time following the well drilling and extensive knowledge about their stratigraphy, hydraulic conductivity and the location of open and closed fractured. Moreover, drawdown could easily be monitored and kept to a minimum during sampling, ensuring minimal degassing and reproducible sampling conditions throughout the monitoring program.

Nonetheless, drilling observation wells is a costly exercice and hence does not allow the same number of wells to be sampled than when also using residential wells. Furthermore, with some of our observation wells, the first results in the timeseries were somewhat different from subsequent results, indicating that caution should be taken when interpreting results from the first sampling campaign(s) for a newly drilled well in a tight rock aquifer. In particular, alkane concentrations can decrease during the first few months if the tight rock in which the wells are drilled contains important amounts of trapped gas. As the tight aquifer is drilled (and thus “broken”), light hydrocarbons, either from microbial or thermogenic origin, can escape from the isolated rock pores close to the borehole walls for a certain period of time, with implications on the identification of gas origin and concentrations in the free-flowing groundwater. This overall effect will be more pronounced in the case of hydrocarbon volatiles-rich rocks, such as those from Lotbinière and Les Fonds formations in our study area.

Groundwater with high concentration of dissolved gases will loose some of its hydrocarbon content through degassing while being pumped or pulled up to the ground surface at atmospheric pressure. Therefore, analyses of gas-charged (effervescing) groundwater sampled with a semi-closed system do not provide concentrations representative of *in situ* conditions and should not be considered as true values, but only as a lower estimate of the downhole concentrations (Molofsky et al., 2016b). Degassing is expected to be more pronounced as gas concentrations increase. Therefore, it is likely that the highest methane concentrations in our wells are underestimated, which may lead to an underestimation of the temporal variations. In spite of this, temporal variations are clearly significant and should be considered in sampling protocols used to establish the range of methane concentrations and isotopic ratios representative of baseline conditions prior to shale gas development.

Indeed, results from this study showed that methane concentrations over time varied by 2.5 to 6 times relative to the smallest recorded value at a given well, and variations largely exceeded the uncertainty arising from sampling, handling and analysis. Hence, performing a single baseline or background sampling campaign in a limited number of wells or over a too strictly regulated distance from a proposed hydrocarbon well cannot capture natural methane variations and could be misleading. Our study showed that the knowledge of temporal natural variability in methane concentrations, and of its magnitude, as well as fluctuations of the carbon and hydrogen stable isotope ratios of the system components (CH_4 and DIC) are crucial in the interpretation of baseline water-quality data. Such a complete baseline information should be available to meaningfully compare against data acquired after initiation of oil and gas production activities, to determine if these activities have affected the groundwater quality.

The set of stable isotope compositions ($\delta^{13}C\text{-}CH_4$, $\delta^{2}H\text{-}CH_4$, $\delta^{13}C$-DIC) included in our monitoring program provided highly valuable information. Carbon isotope ratios of methane ($\delta^{13}C\text{-}CH_4$) were more consistent over time than concentrations in most wells. This agrees with the results from Humez et al. (2015) who monitored a well over 8 years in Alberta (Canada) and from Sherwood et al. (2016), who have used 110 data pairs from the Colorado State database (called COGCC) that spanned over up to 16 years. While we made similar observations in most of our wells, we did observe important variations in the $\delta^{13}C\text{-}CH_4$ values in time-series from two wells. These variations occurred in the two wells with the lowest methane concentrations, i.e. where small changes in gas sources or processes are more likely to be recorded in the carbon isotopic ratios. In these cases, other geochemical parameters were necessary to explain some of the variations. For instance, mixed thermogenic and microbial gas sources, methane oxidation and the presence of microbial gas from an old, deep and isolated groundwater system were identified through the combined use of dryness ratio, $\delta^{13}C\text{-}CH_4$, $\delta^{2}H\text{-}CH_4$, $\delta^{13}C$-DIC and the presence of a young component in the groundwater (indicative of active recharge), as indicated by tritium. This information is crucial for understanding the processes affecting methane in a given well and to detect an eventual oil and gas industry-related change in gas concentration and source in groundwater. The monitoring of DIC isotopes ratios over time, while not common practice in methane baseline studies, is particularly valuable if the exploited gas unit in a region contains mainly microbial gas rather than thermogenic gas. In this case, fugitive gas migrating, for instance, from a faulty casing into shallow aquifers would not contain ethane and propane and could have similar $\delta^{13}C-CH_4$ values as the gas being locally produced by microorganisms in the shallow aquifer. However, this gas could be associated with water with a distinct $\delta^{13}C$-DIC signature that could point to its distinct origin.

To provide the best representative picture of the pre-development conditions that could reliably be used for investigations on potential impacts of oil and gas development activities, we suggest that monitoring be carried out several times over a period of at least a year, or even two years if possible. The first sampling event should include a complete set of organic and inorganic geochemical parameters and ideally all sampling events should include the analysis of alkane (methane, ethane, propane) concentrations, as well as stable isotope analyses of methane ($\delta^{13}C-CH_4$, $\delta^{2}H-CH_4$) and dissolved inorganic carbon ($\delta^{13}C$-DIC). Even if ethane and propane concentrations and isotopic composition could provide excellent indications of gas source variations over time, they are rarely present in sufficient concentration for detailed unequivocal analysis in pre-development groundwater baseline studies, or when there is no gas leak (Baldassare et al. 2014; Moritz et al. 2015; Humez et al. 2015; 2016; Molofsky et al. 2016a).

6 Conclusions

Dissolved methane can be naturally present in shallow aquifers and concentrations can be highly variable spatially and temporally. In this study, temporal natural variations in methane concentrations and isotopic composition were assessed in seven wells (two residential and five dedicated observation wells) in the Saint-Édouard area of the St. Lawrence Lowlands, southern Québec, Canada, prior to any large-scale hydraulic fracturing activities. These wells were sampled at a frequency varying between four and eleven times a year, over a period of up to 2.5 years.

Results demonstrated that even in the absence of industrial hydrocarbon activity, methane concentrations in monitoring wells can vary by several times the smallest recorded values. Methane isotopic composition ($\delta^{13}C$ and $\delta^{2}H$) proved to be more stable and reliable, with variations in most wells being within the relatively low uncertainty expected from sampling, handling and analysis. However, significant temporal variations for both $\delta^{13}C$ and $\delta^{2}H$ were observed in a few wells. A more thorough investigation of the monitoring wells using additional inorganic geochemical parameters showed that even within this small (500 km^2) region, the geological, hydrogeological and geochemical contexts all had impacts, to various degrees, on the magnitude and patterns of variations in methane concentrations and isotopic composition of methane and DIC. Understanding the specific context of each well is critical for distinguishing natural variations from potential anthropogenic contamination.

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References

Alperin MM, Reeburgh WS, Whiticar MJ (1988) Carbon and hydrogen isotope fractionation resulting from anaerobic methane oxidation. Global Biogeochemical Cycles 2: 279-291.

Baldassare FJ, McCaffrey MA, Harper JA (2014) A geochemical context for stray gas investigations in the northern Appalachian Basin: Implications of analyses of natural gases from Neogene-through Devonian-age strata, AAPG Bulletin, 98(2):341-372.

Barker JF, Fritz P (1981) The occurrence and origin in some groundwater flow systems, Canadian Journal of Earth Sciences, 18(12): 1802-1816.

Birdsell DT, Rajaram H, Dempsey D, Viswanathan HS (2015) Hydraulic fracturing fluid migration in the subsurface: A review and expanded modeling results. Water Resources Research, 51: 7159–88, doi: 10.1002/2015WR017810.

Bordeleau G, Rivard C, Lavoie D, Mort A, Ahad, J Malet X, Xu X (2015) Identifying the source of methane in groundwater in a ‘virgin’ area with regards to shale gas exploitation: a multi-isotope approach, conference proceeding, 11th AIG meeting, September 21-25 2015, Orléans, France.

Bordeleau G, Rivard C, Lavoie D, Lefebvre R, Ahad J, Xu X (2017) Identifying the source of methane and higher alkanes in groundwater of the St. Lawrence Platform, Saint-Édouard area, eastern Canada: a multi-isotope approach, conference proceeding, 12th AIG meeting, October, Boulder, Colorado.

Bureau of Land Management and Colorado Oil and Gas Conservation Commission (1994) Groundwater monitoring San Juan Basin, La Plata County, Colorado: Comprehensive infill testing including data obtained in the Pine River Fruitland Coal Outcrop investigative study, Final Report with tables and appendices, 102 p.

Cheung K, Mayer B (2009) Chemical and Isotopic Characterization of Shallow Groundwater from Selected Monitoring Wells in Alberta: Part 1: 2006-2007. Report prepared for Alberta Environment, 76 pages, http://www.assembly.ab.ca/lao/library/egovdocs/2009/alen/173473.pdf

Clark TH (1955) Rapport géologique 66 – Région de St-Jean-Beloeil, Ministère des Mines de la province de Québec, Service de la carte géologique, 2 maps, 92 p.

Clark I, Fritz P (1997) Environmental Isotopes in Hydrogeology, Boca Raton, FL: CRC Press. 328.

Coleman NP, McElreath D (2012) Short-term Intra-Well Variability in Methane Concentrations from Domestic Well Waters in Northeastern Pennsylvania, AAPG Search and Discovery Article #90154©2012, AAPG Eastern Section Meeting: Stray Gas Incidence & Response Forum, Cleveland, Ohio, 24-26 July 2012, http://www.gwpc.org/sites/default/files/event-sessions/Coleman_Nancy.pdf.

Crow H, Ladevèze P (2015) Downhole geophysical data collected in 11 boreholes near St.-Édouard-de-Lotbinière, Québec. Geological Survey of Canada, Open File 7768: 48 pages. doi: 10.4095/297047.

Darrah TH, Vengosh A, Jackson RB, Warer NR, Poreda RJ (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 of the United States of America (PNAS), 111(39): p. 14076-14081.

Dusseault M., Jackson R. (2014) Seepage pathway assessment for natural gas to shallow groundwater during well stimulation, in production, and after abandonment. Environmental Geosciences, 21(3):107-126.

Gassiat C, Gleeson T, Lefebvre R, McKenzie J (2013) Hydraulic fracturing in faulted sedimentary basins: Numerical simulation of potential contamination of shallow aquifers over long time scales. Water Resources Research 49: 8310-8327 DOI 10.1002/2013wr014287.

Golding, S.D., Borehamb, C.J., Esterle, J.S. (2013) Stable isotope geochemistry of coal bed and shale gas and related production waters: A review, International Journal of Coal Geology, 120: 24-40.

Gorody A W (2008) Recommended sampling, analysis, and reporting protocols for baseline groundwater sampling in advance of coalbed gas development in the Telkwa coal field, British Columbia, prepared for the B. C. ministry of Energy, Mines and petroleum Resources, CPG-9798, 39 pages. http://www.universalgeoscience.com/images/2008_Gorody_Recommended_CBG_groundwater_sampling_protocols_BC_MEMPR.pdf

Gorody AW, Baldwin D, Scott C (2005) Dissolved methane in groundwater, San Juan Basin, La Plata County Colorado: Analysis of data submitted in response to COGCC orders 112-156 & 112 -157, November 2005 IPEC Conference, Houston, TX, 14 pages.

http://ipec.utulsa.edu/Conf2005/Papers/Gorody_DISSOLVED_METHANE_IN_GROUNDWATER.pdf

Gorody AW (2012) Factors affecting the variability of stray gas concentration and composition in groundwater, Environmental Geosciences, 19(1): 17–31.

Grossman EL, Cifuentes LA, Cozzarelli IM (2002) Anaerobic methane oxidation in a landfill-leachate plume. Environmental Science and Technology 36: 2436-2442.

Hamblin AP (2006) The “Shale Gas” concept in Canada: a preliminary inventory of possibilities. Geological Survey of Canada, Open File Report 5384: 103 p.

Harkness JS, Darrah TH, Warner NR, Whyte CJ, Moore MT, Millot R, Kloppmann W, Jackson RB, Vengosh A (2017) The geochemistry of naturally occurring methane and saline groundwater in an area of unconventional shale gas development, Geochumica and Cosmochimica Acta, 208: 302-334.

Hirsche T, Mayer B (2009) A comprehensive literature review on the applicability of free and dissolved gas sampling for baseline water well testing. Report prepared for Alberta Environment, 47 pages, http://www.waterforlife.alberta.ca/documents/ApplicabilityFreeDissolvedGas-Mar2009.pdf

Humez P, Mayer B, Inga J, Nightingale M, Becker V, Kingston A, Akbilgic O, Taylor S (2016) Occurrence and origin of methane in groundwater in Alberta (Canada): Gas geochemical and isotopic approaches, Science of the Total Environment 541: 1253-1268.

Humez P, Mayer B, Nightingale M, Ing J, Becker V, Jones D (2015) An 8-year record of gas geochemistry and isotopic composition of methane during baseline sampling at a groundwater observation well in Alberta (Canada). Hydrogeology Journal, DOI: 10.1007/s10040-015-1319-1.

Interstate Technology & Regulatory Council (2007) Protocol for Use of Five Passive Samplers to Sample for a Variety of Contaminants in Groundwater, Technical and Regulatory Guidance, 121 p. http://www.itrcweb.org/GuidanceDocuments/DSP-5.pdf

Jackson RE, Heagle DJ (2016) Sampling domestic/farm wells for baseline groundwater quality and fugitive gas, Hydrogeology Journal, doi 10.1007/s10040-016-1369-z.

Jackson RE, Gorody AW, Mayer B, Roy JW, Ryan MC, Van Stempvoort DR 2013. Groundwater protection and unconventional gas, extraction: The critical need for field-based hydrogeological research, Groundwater, 51 (4): 488–510.

Kennedy GW, Drage J (2015) Assessing patterns of dissolved methane in shallow aquifers related to Carboniferous and Triassic sedimentary basins, Nova Scotia, Canada, ATLANTIC GEOLOGY 51,:233-241, doi: 10.4138/atlgeol.2015.009.

Kinnaman FS, Valentine DL, Tyler SC (2007) Carbon and hydrogen isotope fractionation associated with aerobic microbial oxidations of methane, ethane, propane and butane. Geochimica et Cosmochimica Acta 71: 271-283.

Ladevèze P, Rivard C, Lefebvre R, Lavoie D, Parent M, Malet X, Bordeleau G, Gosselin JS (2016) Travaux de caractérisation hydrogéologique dans la plateforme sédimentaire du Saint-Laurent, région de Saint-Édouard-de-Lotbinière, Québec, Dossier public 8036, 2016; 112 pages, doi:10.4095/297891.

Lavoie D (2008) Appalachian Foreland Basin of Canada, in Sedimentary Basins of the World, Edited by A. Miall, Elsevier, 65-103.

Lavoie D, Asselin E (1998) Upper Ordovician facies in the Lac Saint-Jean outlier, Québec (eastern Canada): palaeoenvironmental significance for Late Ordovician oceanography. Sedimentology, 45: 817-832.Lavoie D, Hamblin AP, Thériault R, Beaulieu J, Kirkwood D (2008) The Upper Ordovician Utica Shales and Lorraine Group flysch in southern Québec: tectonostratigraphic setting and significance for unconventional gas. Geological Survey of Canada, Open File 5900: 56 p.

Lavoie D, Rivard C, Lefebvre R, Séjourné S, Thériault R, Duchesne MJ, Ahad JME, Wang B, Benoit N, Lamontagne C (2014) The Utica Shale and gas play in southern Quebec: Geological and hydrogeological syntheses and methodological approaches to groundwater risk evaluation. International Journal of Coal Geology, 126: 77–91.

Lavoie D, Pinet N, Bordeleau G, Ardakani OH, Ladevèze P, Duchesne MJ, Rivard C, Mort A, Brake V, Sanei H, Malet X (2016) The Upper Ordovician black shales of southern Quebec (Canada) and their significance for naturally occurring hydrocarbons in shallow groundwater. International Journal of Coal Geology, 158: 44-64.

LeDoux St. Thomas M, Szynkiewicz A, Faiia AM, Mayes MA, McKinney ML, Dean WG (2016) Chemical and isotope compositions of shallow groundwater in areas impacted by hydraulic fracturing and surface mining in the Central Appalachian Basin, Eastern United States, Applied Geochemistry, 71: 73-85.

Loomer DB, MacQuarrie KTB, Bragdon I, Connor DA, Loomer HA, Leblanc JF, Nason B (2016) A baseline assessment of private well water quality in areas of potential shale gas development in New Brunswick: Final report Final report for the New Brunswick Energy Institute http://www.nbenergyinstitute.ca/sites/default/files/UNBBaselineGroundwaterReport_Final%20(1).pdf

Martini AM, Walter LM, Budai JM, Ku TCW, Kaiser CJ, Schoell M (1998) Genetic and temporal relations between formation waters and biogenic methane: Upper Devonian Antrim Shale, Michigan Basin, USA, Geochimica et Cosmochimica Acta, 62 (10): 1699–1720, 1998.

Martini AM, Walter LM, Ku TCW, Budai JM, McIntosh, JC, Schoell M (2003) Microbial production and modification of gases in sedimentary basins: A geochemical case study from a Devonian shale gas play, Michigan basin, AAPG Bulletin, 87(8): 1355-1375.

Mauter MS, Alvarez PJJ, Burton A, Cafaro DC, Chen W, Gregory KB, Jiang G, Li Q, Pittock J, Reible D, Schnoor JL (2014) Regional Variation in Water-Related Impacts of Shale Gas Development and Implications for Emerging International Plays. *Environmental Science & Technology*, 48: 8298−8306.

McIntosh JC, Grasby SE, Hamilton SM, Osborn SG (2014) Origin, distribution and hydrogeochemical controls on methane occurrences in shallow aquifers, southwestern Ontario, Canada, Applied Geochemistry, 50: 37-52.

Molofsky LJ, Connor JA, McHugh TE, Richardson SD, Woroszlyo C, Alvarez PJ (2016a) Environmental Factors Associated With Natural Methane Occurrence in the Appalachian Basin, Ground Water, p. 1-13. doi: 10.1111/gwat.12401.

Molofsky LJ, Connor JA, Wylie AS, Wagner T, Farhat SK (2013) Evaluation of methane sources in groundwater in northeastern Pennsylvania: Groundwater, v. 51, no 3, p. 333–349.

Molofsky LJ, Richardson SD, Gorody AW, Baldassare F, Black JA, McHugh TE, Connor JA (2016b) Effect of Different Sampling Methodologies on Measured Methane Concentrations in Groundwater Samples, Ground Water, 24: 1-12, doi: 10.1111/gwat.12415.

Moritz A, Helie JF, Pinti DL, Larocque M, Barnetche D, Retailleau S, Lefebvre R, Gelinas 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 2015, 49. Environmental Science & Technology, 2015, 49, 4765−4771.

Nicot, JP, Larson T, Darvari R, Mickler P, Slotten M, Aldridge J, Uhlman K, Costley R (2017) Controls on Methane Occurrences in Shallow Aquifers Overlying the Haynesville Shale Gas Field, East Texas, Gound Water doi: 10.1111/gwat.12500

Ryan C, Alessi D, Mahani AB, Cahill A, Cherry J, Eaton D, Evans R, Farah N, Fernandes A, Forde O, Humez P, Kletke S, Ladd B, Lemieux JM, Mayer B, Mayer KU, Molson J, Muehlenbachs L, Nowamooz A, Parker B (2015) Subsurface Impacts of Hydraulic Fracturing: Contamination, Seismic Sensitivity, and Groundwater Use and Demand Management, Canadian Water Network, CWN HF-KI Subsurface Impacts Report, 149 pp.

Sharma S, Bagget JK (2011) Application of carbon isotopes to detect seepage out of coalbed natural gas produced water impoundments, Applied Geochemistry 26: 1423–1432.

Sharma S, Mulder ML, Sack A, Schroeder K, Hammack R (2013) Isotope Approach to Assess Hydrologic Connections During Marcellus Shale Drilling, Groundwater, 52(3): 424-433, doi: 10.1111/gwat.12083.

Sherwood OA, Rogers JD, Lackey G, Burke TL, Osborn SG, Ryan JN (2017) Groundwater methane in relation to oil and gas development and shallow coal seams in the Denver-Julesburg Basin of Colorado, PNAS, 113(30): 8391–8396, http://www.pnas.org/content/113/30/8391.full.Siegel DI, Azzolina NA, Smith BJ, Perry AE, Bothun RL (2015) Methane concentrations in water wells unrelated to proximity to existing oil and gas wells in Northeastern Pennsylvania. Environmental Science & Technology, 49(7): 4106–4112.

Siegel D, Smith B, Perry E, Bothun R, Hollingsworth M (2016) Dissolved methane in shallow groundwater of the Appalachian Basin: Results from the Chesapeake Energy predrilling geochemical database, Environmental Geosciences, 23(1): 1-47.

Smith B, Becker M, Siegel D (2016) Temporal variability of methane in domestic groundwater wells, northeastern Pennsylvania, Environmental Geosciences, 23(1): 49–80.

U.S. Department of the Interior (2001) Technical measures for the investigation and mitigation of fugitive methane hazards in areas of coal mining, Office of Surface Mining Reclamation and Enforcement, 124 p. http://www.osmre.gov/resources/library/ghm/methane.pdf

Whisman C, Wardrop R, Good D, McElreath D, Olmsted C, Smith B (2012) Real-Time Monitoring System for Evaluating Long-Term Variability of Methane In Domestic Water Wells In Pennsylvania, AAPG Search and Discovery Article #90154©2012 AAPG Eastern

Section Meeting, Cleveland, Ohio, 22-26 September 2012, http://www.gwpc.org/events/gwpc-proceedings/2012-stray-gas-incidence-response-forum.

Whiticar MJ (1999) Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane, Chemical Geology, 161: 291–314.