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Identifying the source of methane in groundwater in a 'virgin' area with regards to shale gas exploitation: a multi-isotope approach

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Abstract

The Upper Ordovician Utica Shale located in the St. Lawrence Lowlands (Quebec, Canada) represents a promising reservoir of unconventional gas, which is still 'virgin' with respect to fracking due to a *de facto* moratorium. A project was initiated in order to evaluate the vulnerability of shallow groundwater with respect to potential future activities carried out at depth. The geochemical aspect of the project, relying on isotopes of various compounds from shallow groundwater and rock samples, will help establish baseline gas concentrations in the aquifer, evaluating whether gas concentrations and isotopic ratios vary over time, and identifying the source(s) of methane.

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Keywords: shale gas; methane origin; groundwater; fracking, Utica Shale

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1. Introduction

In the last few years, there has been much debate about the risks that shale gas activities pose to groundwater quality in shallow aquifers[1-2]. Several studies have investigated possible migration pathways between deep thermogenic gas reservoirs and shallow aquifers, notably using methane stable isotopes ($\delta^{13}C$, $\delta^{2}H$) to distinguish thermogenic from microbial gas[2-6]. Most of these studies were carried out in areas where shale gas exploitation has been ongoing for a number of years, and several authors have noted the lack of local pre-exploitation baseline for gas in aquifers, as well as monitoring fluctuations in gas concentrations over time[6-7].

A research project was initiated by the Geological Survey of Canada in 2012 in the St. Lawrence Lowlands, where the Upper Ordovician Utica Shale presents a good potential for unconventional gas exploitation. The Utica Shale is a prime candidate for applying a pre-exploitation approach, as the industry targeted this formation between 2007 and 2010, until a *de facto* moratorium was imposed in the province of Quebec. A total of 28 gas wells were drilled in this shale, of which 18 were hydraulically fractured. Because of this limited number of wells, the Utica Shale is considered a frontier play and, therefore, the St. Lawrence Lowlands are viewed as a "virgin" area with regards to fracking. For this project, the St-Edouard area, located 65 km south-west of Quebec City, was selected because the St-Edouard gas well is the most promising well that was drilled in this formation, and because it is located in a region where several faults are known. Indeed, a natural connection between deep and shallow formations is presumed possible only if permeable vertical discontinuities are present (e.g., faulted zones), providing a migration pathway. The project is multi-faceted and includes geophysical, geomechanical, and hydrogeological components, in addition to an extensive geochemical study.

The geochemical component, which is discussed here, aims to: 1) document the presence of gas (methane, ethane, propane) in groundwater from shallow wells in this region, 2) monitor gas concentrations and isotopes in some of these wells over time, and 3) identify the origin of the gas. The general approach is largely based on the use of isotopes, particularly those of methane ($\delta^{13}C$, $\delta^{2}H$) which have traditionally helped distinguishing biogenic methane, generated microbially at various depths (but most commonly near the surface), from thermogenic methane, produced at greater depth by thermal cracking of kerogen or oil under higher pressure and temperature conditions. This approach works well when these respective sources of gas are mutually exclusive, however, various factors may complicate the interpretation at a given site. For instance, processes such as oxidation may alter the isotopic signature of methane. Moreover, thermogenic gas may be found at shallow depths as hydrocarbon-mature deep geological units are now closer to the surface due to long-term erosion processes. Because of this, it is now well-recognized that the presence of thermogenic gas in drinking water wells does not necessarily indicate migration from deep shale plays targeted by industry to shallow aquifers. However, there is still a lack of information concerning geological characteristics including the isotopic signature of the gas within the rock above 500 to 1000 m depth and a lack of methodology for the interpretation of mixed isotopic signatures in groundwater. This situation demands the use of a wider series of isotopes in both water and shallow core samples, in order to better understand the origin of natural gas in aquifers.

2. Methodological approach

The geochemical component of this project involves sampling shallow (<150 m) groundwater from private wells (30) and observation wells drilled for the project (15). Most wells were sampled between one and three times, while others have been monitored every 2 to 4 months for the last 2 years. Additionally, soil gas samples have been collected, as well as rock cores and cuttings during drilling of our monitoring wells. Water samples have been analyzed for concentrations of major and minor ions and trace metals, as well as C1-C3 alkanes (methane, ethane, propane) and volatile organic compounds (VOCs). Some samples were selected for various isotopic analyses, either to describe the groundwater flow system (tritium, radiocarbon, $\delta^{18}O$ and $\delta^{2}H$), or to investigate the source of dissolved gases ($\delta^{13}C$ and $\delta^{2}H$ of methane and ethane, $\delta^{13}C$ of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC), as well as ^{14}C of methane and DIC). Gases extracted from headspace of isojars containing either core samples or drill cuttings were analyzed for C1-C3 alkane concentrations, as well as $\delta^{13}C$ and $\delta^{2}H$ of

methane, ethane and propane, and in some cases, ^{14}C of methane. The intent was to be able to compare chemical and isotopic results between water samples and rock samples that were collected at the same depth, as well as with mudgas samples from the deep Utica Shale, for which gas composition and isotopic data are publicly available.

3. Results and discussion

Results show that methane is present throughout the study area. It was detected in 93% of the sampled wells, at concentrations ranging between the method detection limit (0.006 mg/L) and 40 mg/L. General geochemical results have showed that there are two main groundwater types in the area, namely Ca-HCO_3 and Na-HCO_3, although there are rare occurrences of Na-Cl. The Ca-HCO_3 water type is characterized by low methane compared to the Na-HCO_3 type or Na-Cl type. Wells with Ca-HCO_3 water also tend to be shallower (average depth of 31 m) and contain water of a younger age than wells with Na-HCO_3 (average depth of 55 m) or Na-Cl water (average depth of 110 m).

C1-C3 alkane concentrations have been measured on three occasions in most wells; out of these, six wells (including two residential wells and four monitoring wells) were selected for regular monitoring of gas concentrations and isotopic ratios over a longer period. In the time series, individual concentrations in a given well vary by up to 58% from the mean. One exception is observation well F3 where concentrations have continuously decreased over time, such that only the first value, right after drilling, was above 1 mg/L. Another noteworthy exception is a residential well where methane was present on the first two sampling dates (2.9 and 4.6 mg/L, respectively), but was undetected on the third sampling date. Whether the observed methane concentrations fluctuate on a seasonal basis and/or over short-term is still under investigation. However, for four of the six monitoring wells, the $\delta^{13}C$ and $\delta^{2}H$ ratios of methane show little variation and are more consistent than the concentration data (Fig. 1a). This suggests that isotope monitoring represents a potentially more robust tool for identification of shale gas contamination in drinking water than monitoring methane concentrations alone.

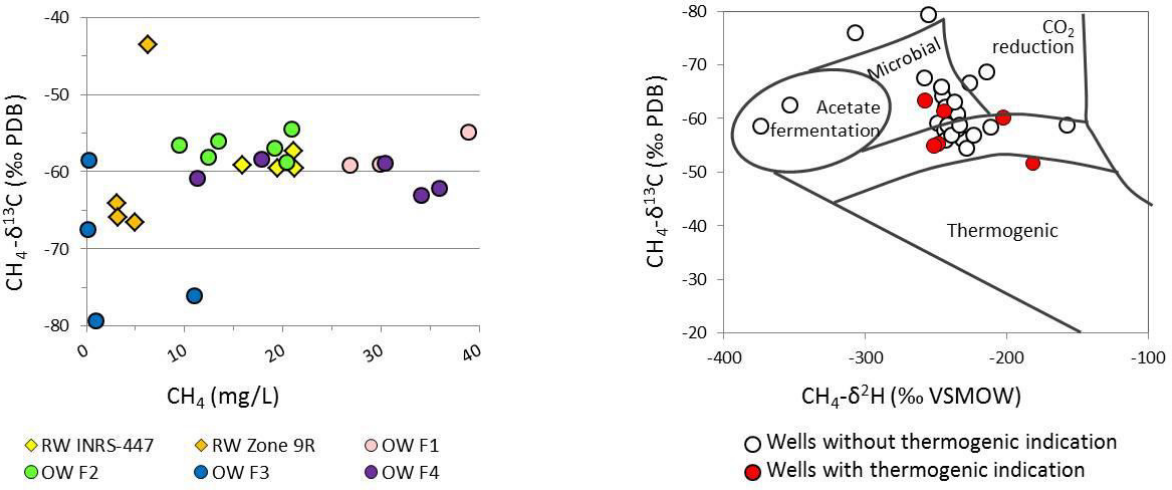

Fig. 1. (a) Methane concentration and $\delta^{13}C$ in all samples collected over a 1.5-year period from the two residential wells (RW) and four observation wells (OW) undergoing long-term monitoring ; (b) Methane $\delta^{13}C$ and $\delta^{2}H$ in all groundwater samples for which both isotopic ratios are available, and general areas defined for thermogenic and microbial gas[8].

For most groundwater samples, the combined methane $\delta^{13}C$ and $\delta^{2}H$ ratios fall in overlap zones between documented ratios for methane of microbial and thermogenic origins (Figure 1b). This observation could be related to various causes, such as mixing of two or more methane types, or methane which has undergone microbial

transformation processes which modified its isotopic ratios[6]. Hence, stable isotopes of methane alone are not sufficient to determine whether there is a contribution of thermogenic and/or microbial methane in these wells. However, other chemical and isotopic data can provide more insight into the origin of methane. For instance, the following indicators for the presence of microbial methane can be used: a dryness index (C1/(C2+C3)) above 1000, DIC-$\delta^{13}C$ values above +10‰, co-variation of CH_4-^{13}C and DIC-$\delta^{13}C$ values, and the presence of ^{14}C in methane. In the St-Edouard project, these factors suggest that microbial methane is ubiquitous in the region. In contrast, factors pointing towards the presence of thermogenic gas, such as significant concentrations of ethane, presence of propane, and/or dry gas index below 100, are found in approximately 25% of the wells (see red symbols on Figure 1b).

While the presence of thermogenic methane in some wells is clear, the indicators discussed above are not sufficient to determine whether this gas comes from the deep Utica Shale reservoir targeted by industry, or rather from the overlying thick sequence of shales of the Lorraine Group, which also constitutes the bedrock aquifer in this region. Stable and radioisotope analyses of the C1-C3 alkanes contained in core samples from some of our observation wells are still under way, but the preliminary data obtained so far indicate that the CH_4-$\delta^{13}C$ values of core and groundwater samples are very similar for a given well, and are different from the values obtained by the industry in rocks at depths of 600 to 2600 m. Therefore, based on geochemical results, the source of the thermogenic gas found in some of the wells is most likely the shallow Lorraine formation.

4. Conclusion

The Upper Ordovician Utica Shale is a promising reservoir of unconventional gas, but public concerns about the vulnerability of shallow groundwater resources in the populated agricultural region of southern Quebec, as well as knowledge gaps identified in the scientific literature, outline the need to conduct pre-exploitation baseline studies. These would allow identifying the origin of methane naturally present in groundwater and its natural variation over time, as well as evaluating whether migration pathways exist between deep gas reservoirs and shallow aquifers that could affect groundwater quality. Preliminary results obtained in this project indicate that methane is ubiquitous in shallow groundwater of the St-Edouard area. While most of the gas seems to be of microbial origin, thermogenic gas is also present in some of the wells, most likely coming from shallow depths where the wells are completed. At the moment, available data from the different project components provide no indication of migration pathways between deep and shallow formations. However, the project is still ongoing and more information, including chemical and isotopic data, is being added, which will help refine the interpretation.

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