ARTICLE IN PRESS

Applied Geochemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Temporal variability of dissolved methane and inorganic water chemistry in private well water in New Brunswick, Canada

Diana B. Loomer[a,*], Kerry T.B. MacQuarrie[a], Tom A. Al[b], Ian K. Bragdon[a], Heather A. Loomer[a,1]

[a] Dept. of Civil Engineering, University of New Brunswick, PO Box 4400, Fredericton, NB, E3B 5A3, Canada
[b] Dept. of Earth and Environmental Science, University of Ottawa, Ottawa, ON, K1N 6N5, Canada

ARTICLE INFO

Editorial handling by Thomas H. Darrah

Keywords:
Methane
Temporal variability
Inorganic chemistry
Groundwater
Shale gas

ABSTRACT

In recent years, there have been a number of studies assessing water chemistry in private water supply wells in areas of unconventional oil and gas development. Many of the wells in these studies were only sampled once and a question remains as to how representative the results from a single sample are given the potential for temporal variability. To evaluate this issue, the temporal variability of water chemistry from fourteen private water wells in two study areas of southeastern New Brunswick was monitored on a monthly basis over the course of a year. The study areas had been the focus of unconventional natural gas development (the Sussex study area) or exploration (the Kent study area). Temporal data for dissolved methane, ethane and propane concentrations, the stable isotopes of carbon and hydrogen in methane, and inorganic chemistry were collected.

In the Kent study area, there was little variation in water chemistry from the six wells studied, with the relative standard deviations (RSD) for methane ranging from 0 to 20%. This indicates that the water from these wells was not affected by seasonal factors such as changing temperature or hydrogeological conditions and that it is possible to acquire reproducible dissolved methane concentrations and water chemistry data from private water supply wells. The drillers' logs for the Kent wells indicate that the casings were installed to depths that likely isolated the water-producing intervals from near-surface hydrogeochemical variations and that the majority of water drawn from the wells enters from a single, relatively high-yield, water-bearing zone. The temporal variability was higher in the eight wells located in the Sussex study area, with the RSDs for methane ranging from 18 to 141%. There were concurrent variations in inorganic parameters, suggesting that the changes in methane concentrations reflected hydrogeochemical fluctuations in the aquifers as opposed to sampling artifacts. The wells with the most variable water chemistry over time had multiple, often relatively low-yield, water-bearing zones. In those wells, methane was associated with Na-HCO_3 water from relatively deep water-bearing zones, while dissolved oxygen (DO) and NO_3 were associated with shallower, Ca-HCO_3, groundwater. The presence of the redox-controlled species Mn, Fe, SO_4 and H_2S, did not appear to affect the temporal variability of methane.

1. Introduction

Unconventional oil and natural gas (ONG) development involves drilling and hydraulic fracturing of low permeability hydrocarbon-bearing geological units. The advancement of these techniques has lead to a surge in unconventional ONG exploration and development. In the United States, unconventional production accounted for less than 1% of the total production in 2007; however, since 2015, extraction from shale-gas or tight-oil formations accounts for > 90% of the country's total ONG production (Ratner and Tiemann, 2015). As a result of public concern about the rapid increase in unconventional ONG development near population centers in the United States, Canada and Europe, regional water quality studies have been implemented in an increasing number of jurisdictions including Nova Scotia, Quebec, Ontario, Alberta, Pennsylvania, New York State, Virginia, North Carolina, England and Germany (Bell et al., 2017; Christian et al., 2015; Darling and Gooddy, 2006; Down et al., 2015; Drage and Kennedy, 2013; Heisig and Scott, 2013; Humez et al., 2016a; McIntosh et al., 2014; McPhillips et al., 2014; Molofsky et al., 2013; Moritz et al., 2015; Schloemer et al., 2016; USGS, 2006). Excluding the studies of Humez et al. (2016a) and Schloemer et al. (2016), who sampled groundwater monitoring wells, the focus of regional studies has been on the detection of dissolved

* Corresponding author.
E-mail address: dloomer@unb.ca (D.B. Loomer).
[1] Present address: Department of Energy and Resource Development New Brunswick, Hugh John Flemming Forestry Centre, P.O. Box 6000, Fredericton, NB, E3B 5H1, Canada.

https://doi.org/10.1016/j.apgeochem.2018.05.003
Received 5 September 2017; Received in revised form 26 February 2018; Accepted 2 May 2018

methane in private water supply wells. The use of private wells allows for regional coverage in areas where there is no existing network of standardized monitoring wells and the costs, both financial and in time, make installing such networks infeasible. There has been debate among the scientific community concerning the validity of using private water supply wells to assess hydrogeochemical conditions (Jackson and Heagle, 2016; McIntosh et al., 2015; Ryan et al., 2015) and while there have been many studies evaluating baseline conditions, to date there has been little information published concerning the reproducibility of the data collected from domestic water wells. Little detailed information is available regarding repeat, or follow-up, sampling of such wells, which leads to questions regarding the representativeness of one-time sampling in determining baseline methane concentrations (CCA, 2014; Jackson and Heagle, 2016; Rhodes and Horton, 2015; Ryan et al., 2015).

Some level of temporal variability of dissolved hydrocarbon gas concentrations is expected (Gorody, 2013); however, the magnitude is not well known. Christian et al. (2015) found differences of approximately 50% in methane concentrations in wells that were resampled in consecutive years. Humez et al. (2016b) also reported differences on the order of 50% in dissolved methane concentrations over an 8-year period from one monitoring well. Temporal monitoring of private water supply wells in the vicinity of unconventional ONG development has been carried out (Hildenbrand et al., 2016; Rhodes and Horton, 2015); however, dissolved methane and other gases such as ethane and propane were not measured. Bell et al. (2017) reported the variability of methane concentrations from quarterly sampling of wells, finding more variability in methane concentrations from wells not in regular use than those in regular use. However, Bell et al. (2017) did not evaluate the dissolved gas concentrations within the context of the inorganic chemistry. The variability of methane concentrations may relate to pumping conditions (Bell et al., 2017) and changing of hydrogeologic conditions such as seasonal water level fluctuations (CCA, 2014). However, methane concentrations may also be impacted by the presence of competitive oxidants common in natural environments including dissolved oxygen (DO) (Magee, 1959; Van Bodegom et al., 2001), nitrate (NO_3) (Haroon et al., 2013; Welte et al., 2016), iron and manganese (Fe(III) and Mn(III,IV)) (Beal et al., 2009) and sulphate (SO_4) (Van Stempvoort et al., 2005). This study aims to evaluate methane variability in private well water within the context of these factors.

From 2014 to 2016, 434 private water wells were sampled in four study areas across southeastern New Brunswick as part of a regional baseline groundwater geochemistry study in areas of recent or potential unconventional ONG development. As part of the study, 14 wells in two of the study areas were monitored monthly over the course of a year to investigate the temporal variability in methane concentrations and inorganic well water chemistry. The objectives of this work are to assess the magnitude of temporal variability of the groundwater geochemistry, in particular, dissolved methane concentrations, and then to examine which hydrogeological, geochemical, or seasonal factors were controlling, or correlated with, the observed temporal variations.

2. Geologic setting

The areas within New Brunswick (NB) that have been targeted for unconventional ONG exploration occur within the Late Paleozoic Maritimes Basin of Atlantic Canada, which is an extensive successor basin that formed as a result of the Early to Middle Devonian Acadian orogeny. In New Brunswick, the Maritimes Basin underlies approximately half the province and is characterized by thick deposits of predominantly sedimentary rocks that were formed in alluvial, fluvial, lacustrine and marine environments. The oldest rocks in the Maritimes Basin are in the Horton Group, followed by five progressively younger sequences: the Sussex, Windsor, Mabou, Cumberland and Pictou groups (St. Peter and Johnson, 2009).

The Horton Group is made up of predominantly alluvial and lacustrine strata and the Sussex Group consists of a sequence of continental clastic rocks that unconformably overlie the Horton Group. The Windsor Group represents a marine incursion and comprises carbonates, gypsum, anhydrite, halite, local potash beds, red mudstones, and coarse-grained clastic rocks. Mabou Group redbeds overlie the Windsor strata. The Cumberland rocks consist of primarily terrestrial coarse conglomerates and sandstones with lesser mudstones and many coal seams. Pictou strata comprise fining-upward fluvial cycles of grey and red sandstones and mudstones with minor coal seams.

The Maritimes Basin represents a horst and graben sequence. The structural trends in New Brunswick are dominated by northeast trending faults with subordinate northwest trending faults (St. Peter and Johnson, 2009; Wilson and White, 2006). The New Brunswick Platform is one of the horsts and there are several deep, northeast-trending grabens, commonly referred to as subbasins, infilled with Horton, Sussex, Windsor and Mabou group rocks. The Cumberland and Pictou groups form a cover sequence that unconformably overlies the older subbasins; the Pictou Group covers most of the New Brunswick Platform. Northeast trending faulting is also recognized in the Pictou group (Van de Poll, 1973), along with secondary north-northwest fault trends (Lefort and Miller, 1999; St. Peter and Johnson, 2009). These pervasive structural trends can be observed in the drainage patterns in New Brunswick (Fig. 1).

In southeastern New Brunswick, the Moncton and Sackville subbasins of the Maritimes Basin have known hydrocarbon resource potential and a history of resource development (Smith et al., 1991). Oil and gas production in New Brunswick extends back into the late 1800's (Martin, 2003), with resource development in the province primarily focused on the Lower Carboniferous lacustrine hydrocarbon-bearing sandstones of the Albert Formation in the Horton Group in the Stoney Creek oil and gas field (Fig. 1). However, in 2000, a natural gas reservoir, the McCully gas field, was discovered at a depth of approximately 2000 m near the town of Sussex (Fig. 1), also in the Albert Formation of the Horton Group. Natural gas extraction from the Hiram Brook sandstone and the Frederick Brook shale members of the Albert Formation has required the use of hydraulic fracturing for stimulation. With the recent advancements in horizontal well drilling, coupled with hydraulic fracturing, it is possible that the natural gas and oil held in the Albert Formation shales may be extracted at economical rates in several other areas throughout the province, and this forms the impetus behind the petroleum industry's exploration activities across southeastern New Brunswick.

3. Study areas

Two study areas (Fig. 2a) were selected based on the location of ONG leases that had been granted by the province of NB as of February 2014. The Kent study area is a low-lying coastal/riverine area extending inland from the shores of the Northumberland Strait. There has been some ONG and coal exploration in the area; however there has been no resource development (St. Peter, 2000). The closest (exploration) ONG well, drilled in 1920, is located > 9 km from a study well (Fig. 2b). The Sussex study area is primarily an agricultural region with a history of potash and limestone mining. Natural gas has been produced from the McCully gas field starting in 2007 and there are historic exploration wells in the area, with drilling records extending back to the early 1900's.

The wells for monthly (time-series) monitoring of groundwater geochemistry were selected from those that had been sampled as part of the regional baseline study. Six wells were selected from the Kent study area and eight from the Sussex study area. None of the wells were located less than 4 km from an ONG well. All wells had standard 15 cm diameter steel casing and were completed as open holes in bedrock, or with slotted casing when completed in unconsolidated sediments. The wells supplied water to individual homes or farm buildings and had