AI PROJECT FINAL REPORT

AI Project Number: #2342 (UofC Ref.: 1037595-1)

1. Geochemical Resource Characterization of Alberta Groundwater

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Project Partners: Alberta Environment and Parks (AEP)

Project Start Date: June 1, 2016
Project End Date: May 31, 2019 with a no-cost extension to August 5, 2019

Report Date: August 13, 2019

2. Executive Summary

Freshwater is required in Alberta to supply safe and secure drinking water for a growing population, to sustain healthy aquatic ecosystems, and for providing quality water for a growing economy. Therefore, an improved understanding of groundwater quality and a geochemical resource characterization of groundwater in Alberta's aquifers is highly desirable. The objective of this project was to advance groundwater resource characterization in Alberta by combining geospatial, geochemical, and isotopic approaches. A total of 278 groundwater samples from GOWN wells throughout the Province of Alberta were collected, and analyzed for the concentrations of major and minor dissolved ions (e.g. Ca, Mg, Na, K, SO_4, NO_3, Cl, DIC (dissolved inorganic carbon)), the concentrations of dissolved gases including methane and ethane, and the isotopic composition of water, nitrate, sulfate, DIC and methane. In addition, groundwater was age dated using ^{14}C of DIC and tritium (^3H).

Age dating of groundwater revealed that the shallow aquifers (<50 m) contain the youngest groundwaters, and are therefore most susceptible to recent anthropogenic contamination from above. In contrast, deeper aquifers (>100 m) contain groundwater that is likely at least hundreds of years old.

The assessment of the hydrogeochemical facies, the redox conditions and the age dating of the samples revealed that young groundwaters are often associated with Ca-HCO_3 and Na-SO_4 water types, have elevated concentrations of sulfate and potentially nitrate, and typically do not contain methane, or if so only in very low concentrations. In contrast, older groundwater samples were found to be associated with Na-HCO_3 and Na-HCO_3-Cl water types, had low sulfate and negligible nitrate concentrations, and contained all the samples with elevated methane concentrations. Hence, the occurrence of elevated methane concentrations in groundwater obtained from GOWN wells was found to be associated with geochemically evolved and highly reducing groundwater that is hundreds to thousands of years old.

Investigation of groundwater contaminants revealed that the majority of groundwater samples from GOWN wells (>87%) contained no nitrate, while the remainder of the samples (12.8%) had nitrate from 1.1 to 260 mg NO_3^-/L with three samples exceed the 10 mg NO_3^--N/L (45 mg NO_3/L) drinking water guidelines. Analysis of the isotopic composition of nitrate for these samples revealed that the sources are a mixture of nitrate derived from manure and synthetic fertilizers inputs after significant N recycling in the agricultural soils, with one sample potentially being impacted by geologically-derived nitrate from glacial tills. Many samples containing nitrate provided evidence of partial denitrification. Hence it was demonstrated that redox conditions for persistence of nitrate in groundwater are only favourable in shallow and young groundwater. In contrast, the more reducing conditions of geochemically evolved, older, and deeper groundwater are not suitable for the occurrence of nitrate.

Many of the obtained groundwater samples contained methane, and isotope analyses revealed that >65% of these samples (>65%) had $\delta^{13}C$-CH_4 values of less than -58 ‰, indicating that this methane is of biogenic origin (e.g. methane is produced by micro-organisms at low temperatures). For the remainder of the methane-containing samples, it was demonstrated that $\delta^{13}C$-CH_4 > -55 ‰ in concert with very low methane concentrations were indicative of oxidation of biogenic methane. A novel geochemical and multi-isotope model was developed that is capable of differentiating between biogenic methane that has been oxidized under aerobic or anaerobic conditions yielding a so-called pseudo-thermogenic signature, and truly thermogenic methane. Application of this model revealed no contamination of aquifers accessed by GOWN wells by deep thermogenic methane. In all cases, methane was found to be of biogenic origin or methane of biogenic origin was partially oxidized frequently coupled with bacterial sulfate reduction.

The application of geochemical and isotopic techniques combined with groundwater dating approaches revealed a systematic evolution that progresses from young, oxidizing Ca-HCO_3 type groundwater in shallow aquifers, which may contain elevated concentrations of nitrate but has at most negligible amounts of methane, towards a more geochemically evolved and much older Na-HCO_3 to Na-(HCO_3)-Cl type groundwater in deeper aquifers. This groundwater contains typically no nitrate but often has elevated concentrations of methane that is of biogenic origin. Hence the project confirmed all three initial hypotheses, namely that:

1. Younger groundwater is generally more oxidizing, whereas older groundwater was found to be highly reducing;
2. Nitrate contamination was detected predominantly in young and shallow groundwater; in contrast elevated methane contents were restricted to deeper and much older groundwater units;
3. There exists an intermediate zone where the reduction of nitrate and sulfate may be coupled to the oxidation of methane.

The logical next step is to conduct a much more expanded investigation that determines the occurrence, origin and fate of aqueous contaminants in Alberta groundwater by incorporating other existing aqueous geochemistry data sets such as the Baseline Well Water Testing (BWWT) database and the groundwater quality data housed in Alberta Health Services (AHS). Such a follow-up project would provide an unprecedented knowledge of the groundwater quality conditions throughout Alberta for the benefit of groundwater users in Alberta.

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4. Project Description

4.1 Introduction and challenge

Freshwater is required in Alberta to supply safe and secure drinking water for a growing population, to sustain healthy aquatic ecosystems, and for providing quality water for a growing economy. Historically, much of the freshwater needs in Alberta have been derived from surface water sources, but approximately 20% of Albertans rely on groundwater for domestic use. Also, continuously increasing freshwater demands by an expanding economy and population in concert with shifting river flows have revealed limitations of the freshwater water supply from surface water sources, especially in the southern parts of the province resulting in some watersheds being closed for new water licenses. To ensure a safe and secure water supply in light of the expected economic and population growth in Alberta over the coming decades, it will be necessary to increasingly rely on groundwater for freshwater supplies. Therefore, an improved understanding of groundwater quality and a geochemical resource characterization of groundwater in Alberta's aquifers are highly desirable.

4.2 Technology or Research description

Combining geospatial, geochemical, isotopic, and groundwater age-dating techniques constitutes an innovative approach to achieve major advances in groundwater resource characterization in Alberta. Combined, these data enabled the research team to test a number of hypotheses that are important for developing a better understanding of the controls on groundwater quality in the Province of Alberta.

4.3 Overall scope and objectives of the project

The objective of this project was to advance groundwater resource characterization in Alberta by combining geospatial, geochemical, and isotopic approaches. The research team assessed spatial and temporal variations in quality, types and redox states of groundwater by continuing and expanding a comprehensive groundwater sampling and analysis program using the provincial GOWN network in collaboration with Alberta Environment & Parks (AEP). This was achieved by pursuing the following sub-objectives:

(1) To determine current water quality and concentrations of key contaminants in Alberta groundwater. These include nitrate and hydrocarbons. Nitrate potentially contaminates aquifers via infiltration after application of synthetic fertilizers or manure. The presence of "stray gases" such as methane, ethane etc. can result from the recovery of unconventional hydrocarbons (e.g. hydraulic fracturing) but they also occur naturally.

(2) To determine the distribution and sources of the key contaminants using chemical and isotopic techniques.

(3) To relate 3D concentrations of the key contaminants to calculated groundwater ages in order to quantify timespans required for contaminants to build up or degrade along groundwater flow networks.

(4) In combination, sub-objectives 1-3 resulted in the development of low-resolution regional maps of Alberta's groundwater resources and their vulnerability to contamination enabling an assessment of the

impact of human activities (fertilization, groundwater withdrawal, hydraulic fracturing) on groundwater quality.

4.4 Work scope overview

Combining geospatial, geochemical, isotopic, and groundwater age-dating techniques is an innovative approach to achieve major advances in groundwater resource characterization in Alberta. Combined, these data enabled the research team to test a number of hypotheses that are important for developing a better understanding of the controls on groundwater quality that include:

Hypothesis 1: younger groundwater has higher oxygen concentrations, whereas anoxia is more common in older and deeper groundwater;

Hypothesis 2: younger groundwater tends to have higher concentrations of labile nutrients such as NO_3, whereas older groundwater has higher concentrations of dissolved gases such as methane and ethane either from biogenic or potentially thermogenic sources;

Hypothesis 3: there exists an intermediate zone where the reduction of oxygen, nitrate or sulfate is likely coupled to the oxidation of methane. Identification of such zones is important since they are key areas for attenuation of potential aquifer contamination with stray gases that may originate from leaky energy wells.

5. Approach and Results

5.1 Sampling Program

A total of 278 groundwater samples from GOWN wells throughout the Province of Alberta (Fig. 1) were collected. The research team obtained 87 groundwater samples in year #1 (2016), 105 groundwater samples in year #2 (2017), and 86 groundwater samples in year #3 (2018). To collect samples representative of aquifer conditions, the groundwater wells were purged until the field parameters, pH, redox, dissolved oxygen, temperature, and electrical conductivity stabilized. After field measurements and preservation of the samples in the field, they were returned to the University of Calgary for aqueous and gas chemical and isotopic analyses.

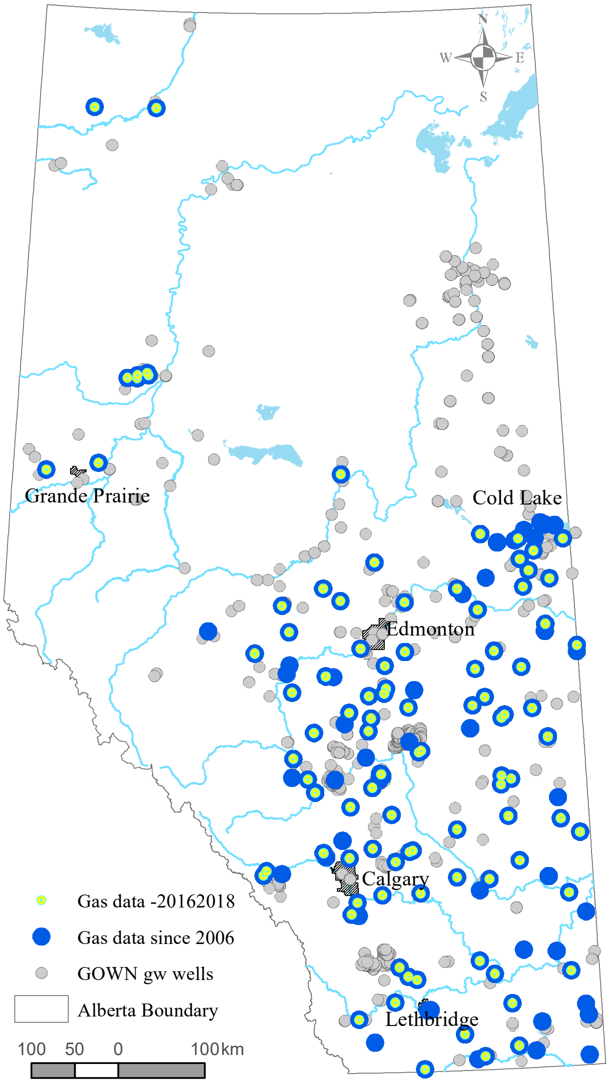

Figure 1: *Inventory of groundwater wells that have been sampled from 2016 to 2018.*

5.2 Analytical methods

In the laboratory, groundwater samples were analyzed for the concentrations of major and minor dissolved ions (e.g. Ca, Mg, Na, K, SO_4, NO_3, Cl, DIC (dissolved inorganic carbon)), the concentrations of dissolved gases including methane and ethane, and the isotopic composition of water, nitrate, sulfate, DIC and methane. In addition, groundwater was age dated using ^{14}C of DIC and tritium (^3H). The generated GOWN database compiled during this project contains aqueous and gaseous geochemical and isotopic data for groundwater samples from122 wells.

5.2.1 Major and minor ion analyses

Alberta Innovates Technology Futures (AITF) conducted the major and minor ion chemistry analyses on filtered samples (0.45µm) that were acidified to $pH < 2$ for cation analysis and non-acidified for major anion determination. ICP-MS analysis was used to determine cation concentrations while titration for alkalinity and ion chromatography were used to determine anion concentrations with analytical uncertainties of ±5%.

5.2.2 Gas composition analyses

A detailed description of the sampling equipment and procedures for dissolved gas samples is given in Humez et al. (2016). The composition of gas samples was determined in the laboratory by gas chromatography yielding concentrations for oxygen, nitrogen, carbon dioxide, methane and higher alkane chain compounds (such as ethane) with measurements conducted by AITF with analytical uncertainties of ±5%.

5.2.3 Stable isotope analyses

Stable isotope compositions of water, DIC, nitrate, sulfate, and the dissolved gases CH_4 and CO_2 were analyzed in the Isotope Science Laboratory at the University of Calgary using standard techniques. Results are reported in the internationally accepted delta notation (δ) where $\delta = (R_{sample}/R_{standard} - 1) \times 1000$ with R_{sample} being the ratio between the heavier and the lighter isotope in the sample, and $R_{standard}$ is the same ratio in a reference material. Delta values are reported in ‰ with respect to internationally accepted standards.

Carbon isotope analyses of dissolved methane and CO_2 were conducted on a ThermoFisher MAT 253 isotope ratio mass spectrometer (IRMS) coupled to a Trace GC Ultra + GC Isolink. The precisions for carbon isotope analyses were $< \pm 0.5$‰ for hydrocarbons and $< \pm 0.2$‰ for carbon dioxide.

5.2.4 Radioactive isotope analyses

Samples for C-14 analysis were sent to the A.E. Lalonde Laboratory at the University of Ottawa for analysis by accelerator mass spectrometry (AMS). Sample pretreatment techniques are described in Crann et al. (2017). Radiocarbon analyses were performed on a 3MV tandem accelerator mass spectrometer built by High Voltage Engineering (HVE).

Reimer et al. (2004) describe the different conventions in radiocarbon measurements for post-bomb ^{14}C data and define a fractionation-corrected fraction modern (the $F^{14}C$ value) according to the amended conventions of Stuiver and Polach (1977):

$$\mathrm{F^{14}C} = \frac{^{14}A_{SN}}{^{14}A_{ON}} \quad (1)$$

where $^{14}A_{SN}$ and $^{14}A_{ON}$ refer to the fractionation-corrected or normalized ^{14}C activity for the sample and the secondary Oxalic acid-II (Ox2) standard used for the ^{14}C-measurements (Crann et al., 2017). Both specific activities of the sample and Ox2 $^{14}A_S$ and $^{14}A_{ox2}$ are first measured and then normalized to a $\delta^{13}C$ value of -25‰ giving the normalized sample activities $^{14}A_{SN}$ and $^{14}A_{ON}$. $F^{14}C$ can range between 0 and 1 (1 for modern value) or 0 to 100% modern carbon.

The conventional radiocarbon age is given by:

$$\mathrm{Age} = -8033 * \ln\left(\mathrm{F^{14}C}\right) \quad (5)$$

with the half-life time $T_{1/2}$ of 5568 years divided by ln(2) resulting in the value 8033. The ^{14}C ages thus calculated are reported in BP or “Before Present”, where the term “present” refers to the standard activity in the year 1950 AD. The measured activity plus error $F^{14}C \pm \sigma(F^{14}C)$ reported can be translated into an age $T \pm \sigma(T)$.

Tritium (^3H) is a radioactive isotope of hydrogen with a half-life of 12.4 years. Tritium concentrations are reported in tritium units (TU) where 1 TU is defined as the presence of one tritium in 10^{18} atoms of hydrogen. From 2016-2017 sampling campaign, tritium was analyzed on 72 groundwater samples at the A.E. Lalonde Laboratory at the University of Ottawa by electrolytic enrichment followed by standard liquid scintillation counting with a precision of 0.8 TU.

5.3 Results

5.3.1 Groundwater age dating measurements

Tritium and carbon-14 measurements on dissolved inorganic carbon (DIC) were conducted on 72 groundwater samples. 22 groundwater samples had tritium concentrations above the detection limit varying from 1.0 to 23 tritium units (TU) indicating that portions of the groundwater were derived from recent recharge (<50 years) (Fig. 2). No tritium above the detection limit was found in 50 groundwater samples suggesting that these waters had recharged prior to 1950.

The ^{14}C-DIC measurements are expressed as fraction modern F^{14}C values that can range between 0 and 1 (1 for modern values) and are reported here as percent (%) modern carbon ranging from 0 to 100%. Ten of 72 samples were below the detection limit for the C-14 method of 0.52 % modern carbon indicating very high groundwater ages. For the remaining 62 samples, F^{14}C activities ranged from 0.61 to 89 % modern carbon with a median value of 24% modern carbon (Fig. 2). ^{14}C-DIC results for triplicate samples from the same well resulted in coefficients of variation ($\sigma/\mu*100$) varying from 0.6 to 2.2% (n_{tripli} =3) indicating good reproducibility and precision of ^{14}C-measurements.

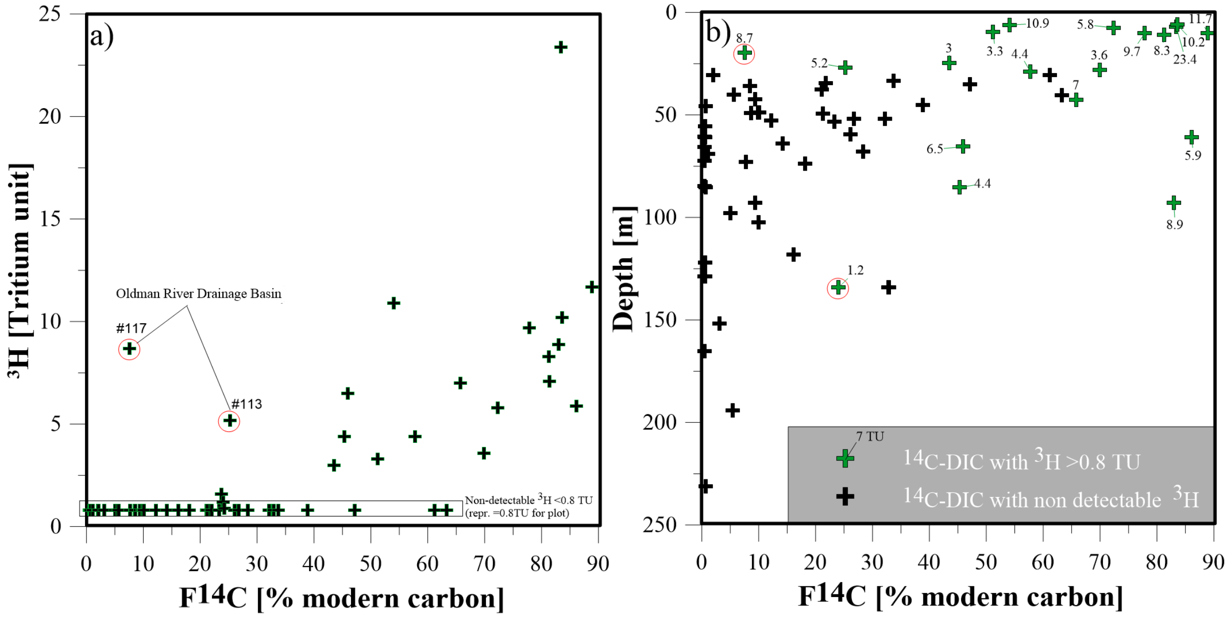

Figure 2: *a) Radiocarbon versus tritium results indicating good correlation between high $^{14}F_{DIC}$ and ^3H contents; b) Age dating distribution versus depth of sampled wells.*

Fig. 2a illustrates that groundwater samples with tritium contents >0.8 TU are associated with higher F^{14}C-DIC values (>40-90% modern carbon) revealing comparatively young groundwater ages or admixture of some recently recharged groundwater. Groundwater samples with F^{14}C-DIC values of less than 40% modern had usually no tritium, indicating considerable groundwater ages of likely several hundred to a few thousand years. Only two samples from wells located in the Oldman River drainage basin with F^{14}C-DIC values of less than 40% modern had also noticeable tritium contents (samples #117 and #113, see Fig. 2a), likely suggesting the mixing of predominantly very old groundwater with a small portion of recently recharged water.

Figure 2b shows ^{14}C and tritium contents plotted versus the depths of the wells from which the groundwater was obtained. Groundwaters with tritium contents >1.0 TU were predominantly observed in shallow wells indicating comparatively young groundwater ages. In GOWN wells deeper than 100 m, tritium was not detectable and $F^{14}C$-DIC values were below 40% modern carbon suggesting that the deeper aquifers contain groundwaters that are hundreds to thousands of years old.

Age dating of groundwater revealed that the shallow aquifers (<50 m) contain the youngest groundwaters, and are therefore most susceptible to recent anthropogenic contamination from above. In contrast, deeper aquifers (>100 m) contain groundwater that is likely at least hundreds of years old.

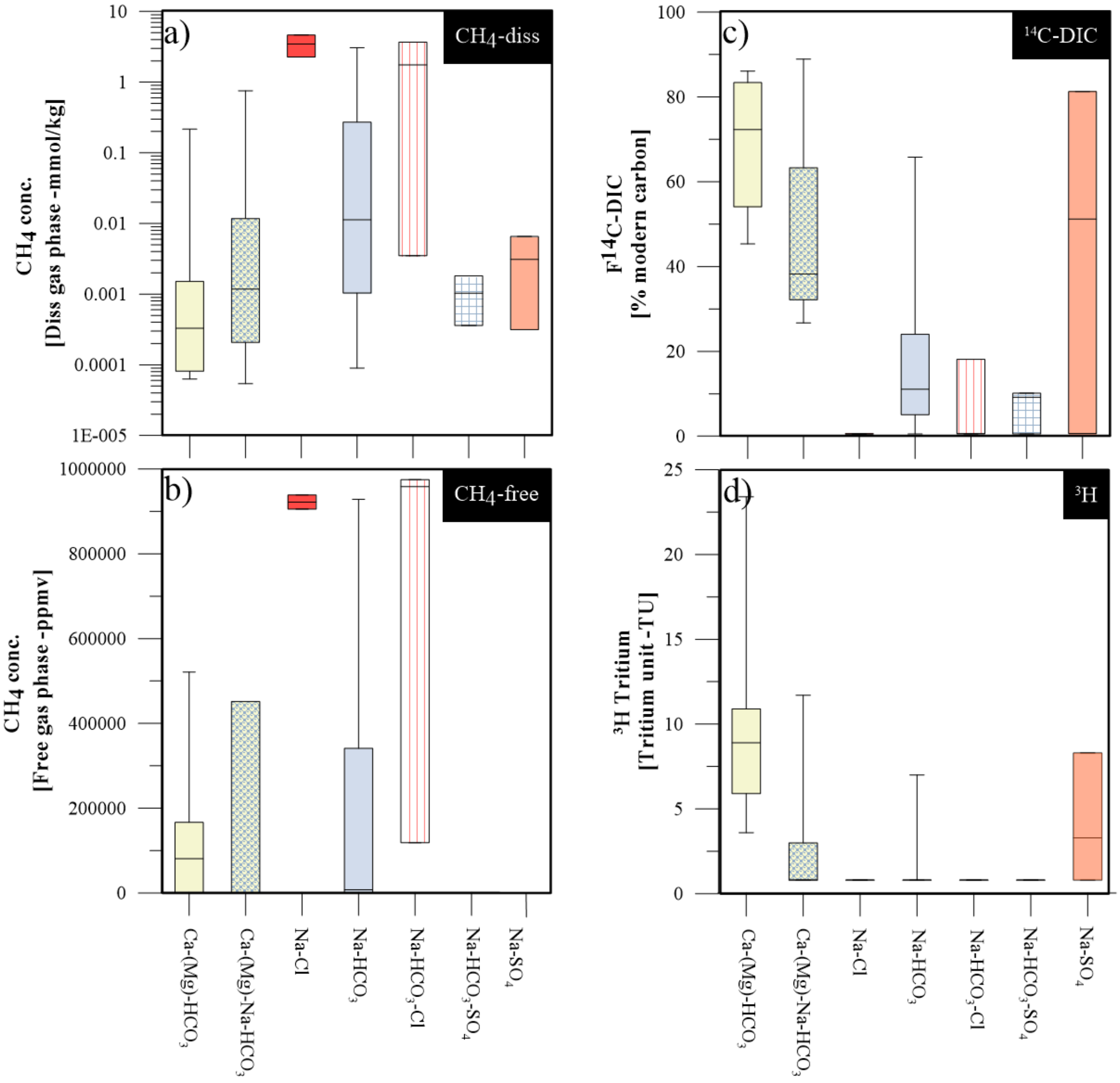

Figure 3: *a) methane concentration in the dissolved gas phase b) methane concentration in the free gas phase c) ^{14}C-DIC activities d) tritium measurements versus water-types.*

5.3.2 Hydrogeochemical facies of groundwater systems, redox zoning and age dating

Based on the concentration data for major anions, cations and several minor ions, the research team determined the predominant water types of the groundwater samples, the redox states of the aquifers, and the occurrence of select groundwater contaminants in dependence of groundwater ages.

5.3.2.1 Hydrogeochemical facies and groundwater age dating data

As revealed by Fig. 3, the obtained groundwater samples had a variety of different water types ranging from $Ca\text{-}HCO_3$ to $Na\text{-}(HCO_3)\text{-}Cl$ water types. $Na\text{-}HCO_3$ was the main water type that represents > 40 % of the groundwater samples. The frequency order for the other water-types (>2%) is as follows: $Na\text{-}HCO_3$ (40.5%) > $Ca\text{-}HCO_3$ (13.8%) > $Ca\text{-}Mg\text{-}HCO_3$ (9.4%) > $Na\text{-}HCO_3\text{-}SO_4$ (8.7%) > $Na\text{-}SO_4$ (5.1%) > $Na\text{-}HCO_3\text{-}Cl$ (4.3%) > $Ca\text{-}Mg\text{-}HCO_3$ (3.6%) ≥ Na-Cl (3.6%) > $Ca\text{-}Na\text{-}HCO_3$ (2.2%). As discussed later in mire detail, $Ca\text{-}HCO_3$ type waters had generally negligible methane concentrations, whereas the highest concentrations of methane were observed in $Na\text{-}HCO_3$, $Na\text{-}HCO_3\text{-}Cl$, and Na-Cl type waters (Fig. 3a,b).

In Figures 3c,d, the groundwater types are plotted versus the age dating parameters tritium and ^{14}C of DIC. It is apparent Ca-rich groundwaters are very young as indicated by high tritium and ^{14}C contents and occur predominantly in shallow aquifers (Fig. 2b). In contrast, Na-rich waters had typically no tritium and very low ^{14}C contents (Fig. 3c,d) and hence were statistically very different ($p<0.05$, Mann Whitney tests). They occur predominantly in deeper aquifers and are geochemically more evolved as a consequence of much higher groundwater residence times. This suggests that groundwater evolves from highly oxidized conditions in shallow aquifers with recently recharged waters to highly reducing conditions in deeper aquifers containing water with residence times of hundreds to thousands of years.

5.3.2.2 Occurrence of electron acceptors and methane in groundwater samples

As groundwater evolves from highly oxidized to highly reducing conditions, it undergoes a sequence of redox reactions including O_2 consumption, denitrification, Mn(IV) and Fe(III) reduction, bacterial sulfate reduction, followed by methanogenesis. Hence, an assessment of the concentrations of dissolved oxygen, nitrate, Mn(II), Fe(II), sulfate and methane provides information about the redox state of groundwater.

Dissolved oxygen concentrations in the Alberta groundwater samples from GOWN wells are consistently <1.0 mg/L, indicating anoxic or post-oxic conditions (Berner, 1981).

The distribution of nitrate concentration in the groundwater samples is highly skewed. More than 87% (n=78) of groundwater samples had concentrations of nitrate lower that <0.2 mg NO_3/L [0.003 mmol/L] indicating that there is no nitrate influx at these locations and/or that denitrification had removed any nitrate. In 12.8% of the samples, nitrate above the detection limit was found with concentrations varying from 1.1 to 260 mg NO_3^-/L [0.02 to 4.2 mmol/L]. Elevated nitrate concentrations were exclusively found in groundwater from wells (Fig. 4). Only three groundwater samples (#219, #3026 and #117) exceed the 10 mg NO_3^--N/L (45 mg NO_3/L) drinking water guidelines. The groundwater sample with the highest nitrate concentration of 260 mg NO_3/L was collected from a well located near Lethbridge (#117) in the Oldman River drainage basin (red symbol, Fig. 2).

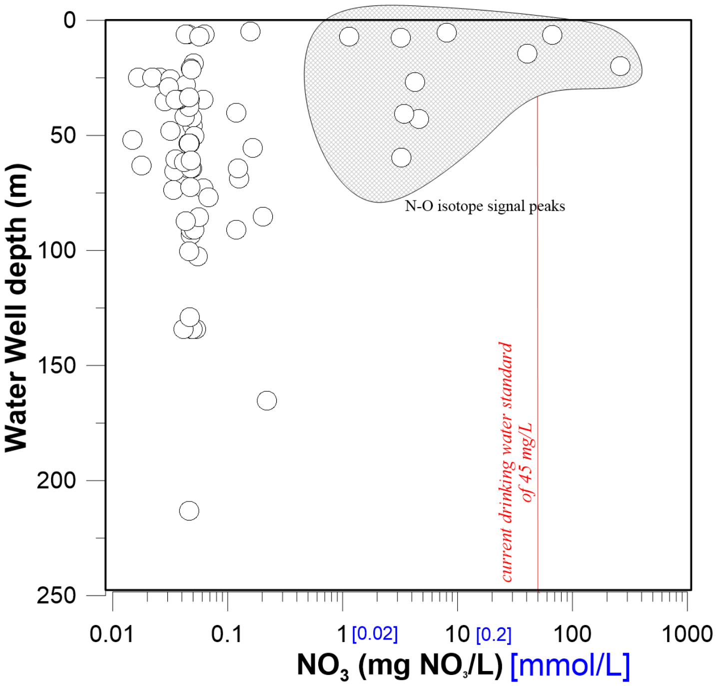

Figure 4: *Well depth versus nitrate concentration in the groundwater samples (2018 sampling campaign)*

Iron and manganese occurred in groundwater from GOWN wells in reduced form (Fe(II) and Mn(II)) and had generally concentrations below 0.01 mmol/L.

In contrast, GOWN groundwaters had for the most part considerable sulfate concentrations that were as high as 9,600 mg/L [100 mmol/L]. Therefore, the main electron acceptor in the groundwater samples from GOWN network was found to be sulfate.

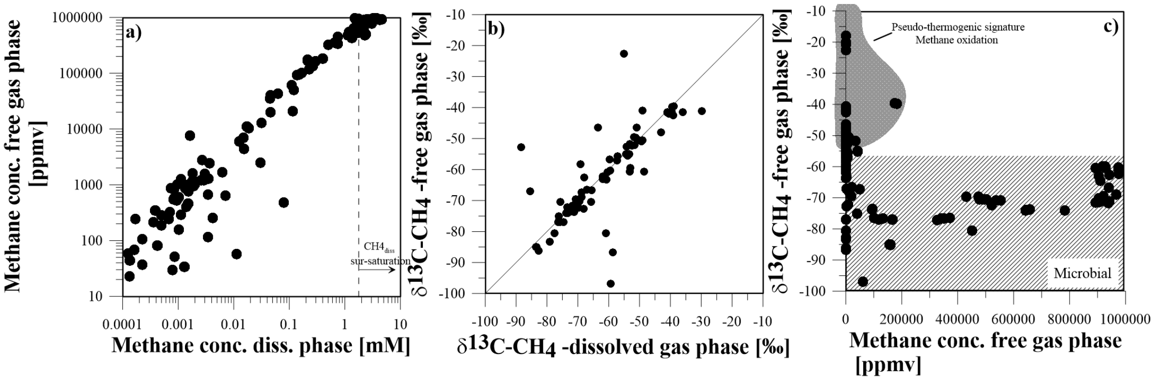

Figure 5: *a) Methane concentrations in both dissolved and free gas phases; b) δ^{13}C values of methane in both dissolved and free gas phases; c) concentrations and C isotope ratios of methane in the free gas phase for GOWN groundwater samples collected between 2016 and 2018.*

Methane is the most reducing species and was found to be ubiquitous in the groundwater samples from the GOWN wells. The concentrations of methane, ethane and other gases were determined for both dissolved and free gas samples (Fig. 5a). In the dissolved gas phase, the methane concentrations varied from 0.3 µg/L [1.88 10^{-5} mM] to >30 mg/L [>1.8 mM] (n=246) and in the free gas phase the methane concentrations varied from <50 ppmv to >900,000 ppmv (n=137). Ethane was detected in less than 20% of all groundwater samples in both dissolved and free gas phases. Propane was detected in less than 10% of all groundwater samples in both dissolved and free gas phases. Figure 5a reveals that there is a strong correlation and good agreement between methane concentrations in free and dissolved gas phases consistent with Henry's law, suggesting that the sampling and analytical approaches are highly reliable and accurate (Fig. 5).

5.3.2.3 Redox zone assessments and prediction of methane occurrence

Based on nitrate (NO_3), sulfate (SO_4) and methane (CH_4) concentrations it was possible to classify the groundwater samples into four redox zones (Fig. 6b):

- Zone I represents groundwater redox conditions with elevated NO_3 (> 0.01 mmol/L) and SO_4 (>1 mmol/L) concentrations;
- Zone II represents groundwater redox conditions with elevated NO_3 (> 0.01 mmol/L) and low SO_4 (<1 mmol/L) concentrations;
- Zone III represents groundwater redox conditions with low NO_3 (< 0.01 mmol/L) and elevated SO_4 (>1 mmol/L) concentrations;
- Zone IV represents groundwater redox conditions with both low NO_3 (< 0.01 mmol/L) and low SO_4 (<1 mmol/L) concentrations.

Low concentrations of NO_3 and SO_4 could be the result of denitrification and bacterial sulfate reduction generating redox conditions suitable for methanogenesis.

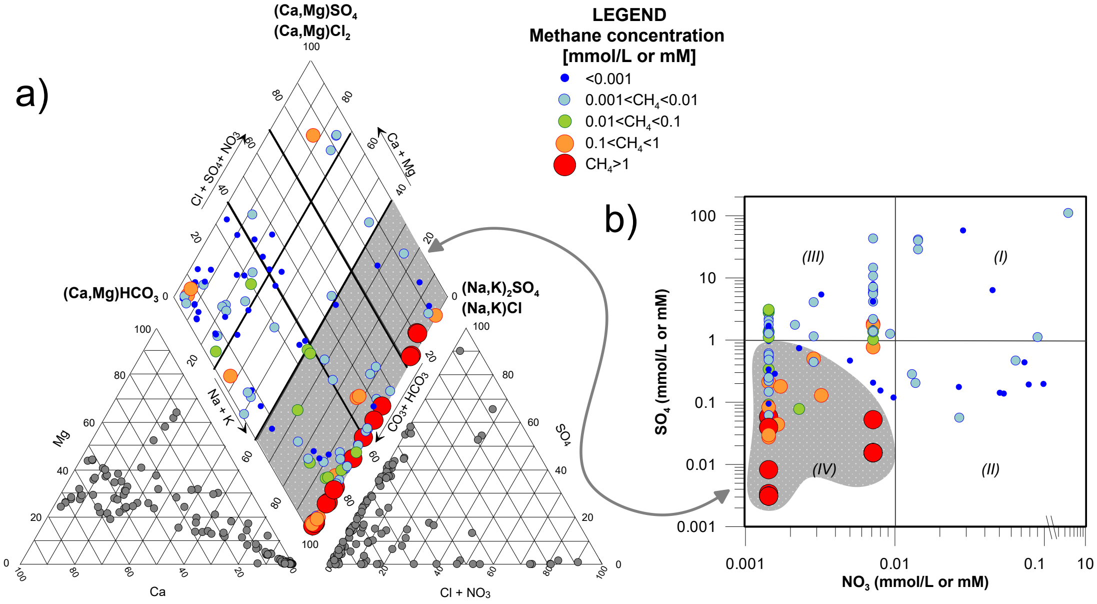

Figure 6: *a) Piper diagram with associated groundwater types for the groundwater samples b) plot of the main electron acceptors present in the groundwater systems. Zone I: elevated NO_3 and SO_4 conc. (low CH_4); Zone II: elevated NO_3 and low SO_4 conc. (low CH_4); Zone III: low/negligible NO_3 and elevated SO_4 conc. (low CH_4); Zone IV low/negligible NO_3 and SO_4 conc. (elevated CH_4). In both figures the methane concentrations are represented with a color code where red colors represent the highest concentrations.*

In zones I, II and III of Figure 6b where nitrate and sulfate concentrations of groundwater are elevated, methane was not detected or only found in negligible concentrations. Elevated methane (CH_4) concentrations in groundwater were observed when the concentrations of nitrate (NO_3) and sulfate (SO_4) were low to negligible (zone IV, Fig. 6b), consistent with the redox ladder concept. Zone IV of Fig.6b contains 100% of the groundwater samples with methane concentrations >1 mmol/L and 85% of samples with methane concentrations >0.01 mmol/L. This suggests that the approach to predict the presence of methane based on the concentrations of NO_3 and SO_4 in groundwater is very promising. Some groundwater samples with elevated methane concentrations occurred in zone III (<15%), indicating that methane is likely in a metastable state. This may be evidence of fugitive methane migrating from deeper strata into shallower and more oxidizing groundwater environments.

Figure 3a reveals that elevated methane concentrations in groundwater are associated with Na-HCO_3 and Na-HCO_3-Cl water types where no tritium was detected and where the uncorrected $F^{14}C_{DIC}$ values are very low (Fig. 7). Hence, Figure 7 reveals that elevated methane concentrations were associated with lowest ^{14}C DIC activities or older groundwater, whereas more modern water associated with elevated tritium concentrations had either no or only negligible methane contents.

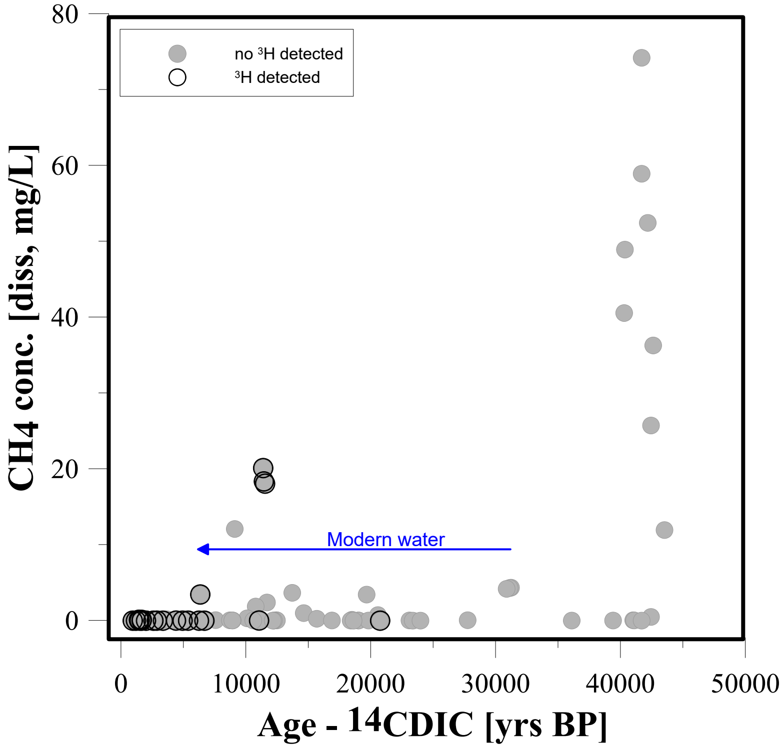

Figure 7: *Relationship between age dating measurements (age non corrected) and methane concentration in GOWN groundwater.*

The assessment of the hydrogeochemical facies, the redox conditions and the age dating of the samples revealed that young groundwaters are often associated with Ca-HCO_3 and Na-SO_4 water types, have elevated concentrations of sulfate and potentially nitrate, and typically do not contain methane, or if so only in very low concentrations. In contrast, older groundwater samples were found to be associated with $Na\text{-}HCO_3$ and $Na\text{-}HCO_3\text{-}Cl$ water types, had low sulfate and negligible nitrate concentrations, and contained all the samples with elevated methane concentrations. Hence, the occurrence of elevated methane concentrations in groundwater obtained from GOWN wells was found to be associated with geochemically evolved and highly reducing groundwater that is hundreds to thousands of years old.

5.4 Analysis of Results and Discussion

5.4.1 Sources and fate of selected contaminants in groundwater

5.4.1.1 Sources of nitrate in groundwater

High nitrate concentrations in water are associated with adverse health effects if the groundwater is used for drinking water purposes. Elevated concentrations of nitrate in groundwater may be linked to various sources of nitrate including synthetic fertilizer and manure applications, septic tank leakage, sewage discharge, oxidation of organically bound nitrogen in soils, or geologically-derived nitrate from glacial till. Data from Alberta Agriculture and Forestry (Government of Alberta) were compiled in maps and show extensive application of synthetic fertilizers and manure in some regions that can be a potential source of nitrate in groundwater (Figures 8a-c). Elevated nitrate concentrations in groundwater were only observed in few GOWN wells that are located in a areas of intensive agriculture with significant application of synthetic fertilizers and/or manure (Figs. 8b,c) resulting in an elevated groundwater quality risk (Fig. 8a). The GOWN wells yielding groundwater with elevated nitrate concentration are predominantly located in the agricultural corridors between Edmonton and Calgary, and Calgary and Lethbridge.

In order to identify sources of elevated nitrate in the shallow aquifers of Alberta and for identifying geochemical processes that may have attenuated the nitrate concentrations, $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values from GOWN groundwater samples were interpreted in concert with concentrations of nitrate and other dissolved groundwater constituents. Figure 9a reveals that nitrate concentrations >10 mg/L were associated with $\delta^{15}N$ values ranging between +8 and +26 ‰ suggesting either manure-derived nitrate sources or geologically-derived nitrate from glacial till. In contrast, some groundwater samples with nitrate concentrations between 2 and 10 mg/L nitrate had lower $\delta^{15}N$ values ranging between +2 and +8‰ indicating a mixture synthetic fertilizer and manure-derived nitrate (Fig. 9a).

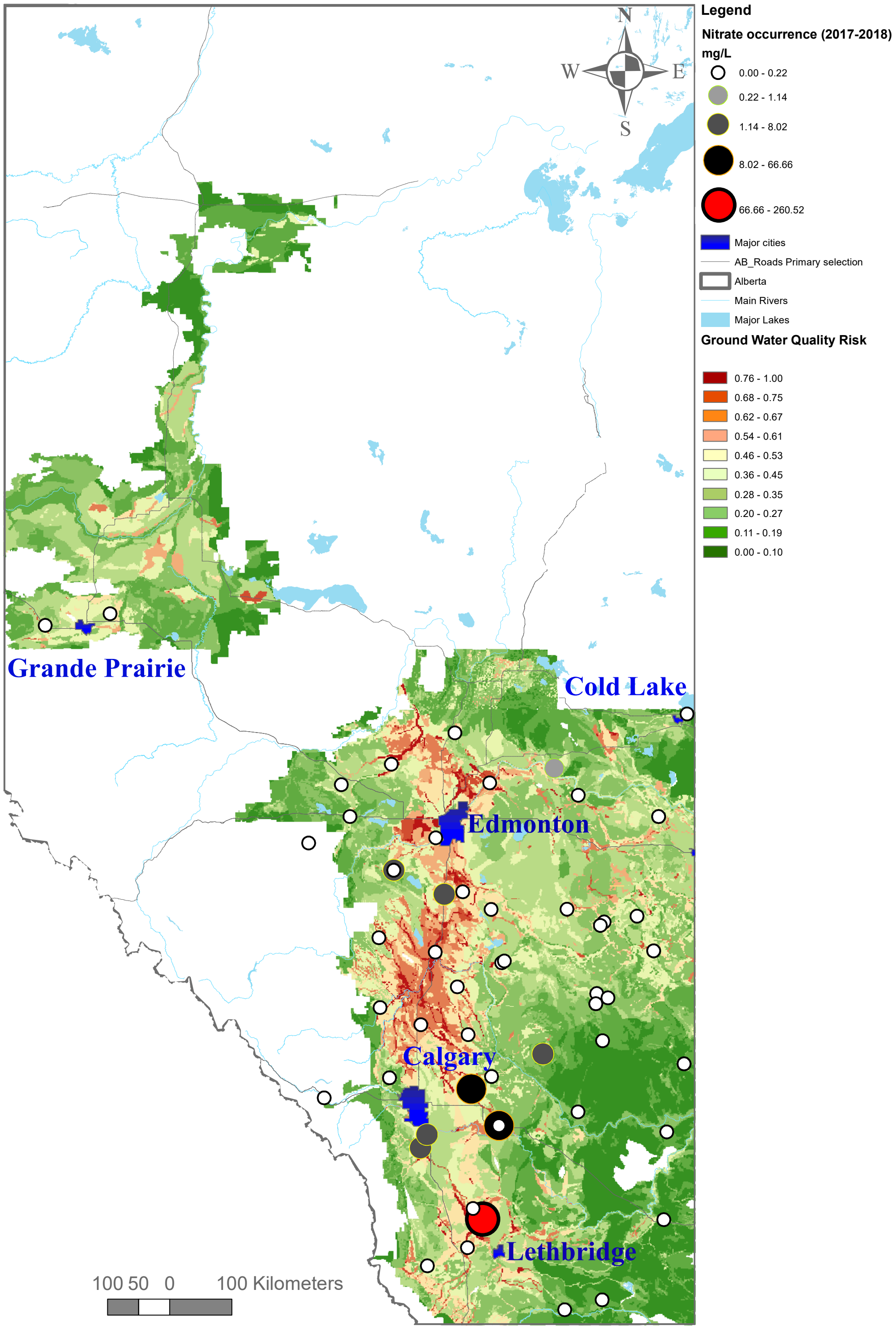

Figure 8a: *Occurrence of nitrate in groundwater samples obtained from GOWN wells in southern Alberta. Under layer displays an assessment of groundwater quality risk for the agricultural area of Alberta. Agricultural activities that may have an impact on groundwater quality include livestock, crop production and agrochemical use. The classes shown on the map were ranked from 0 (lowest risk) to 1 (highest risk) (from Alberta Agriculture and Forestry, Government of Alberta, layer created in 2005).*

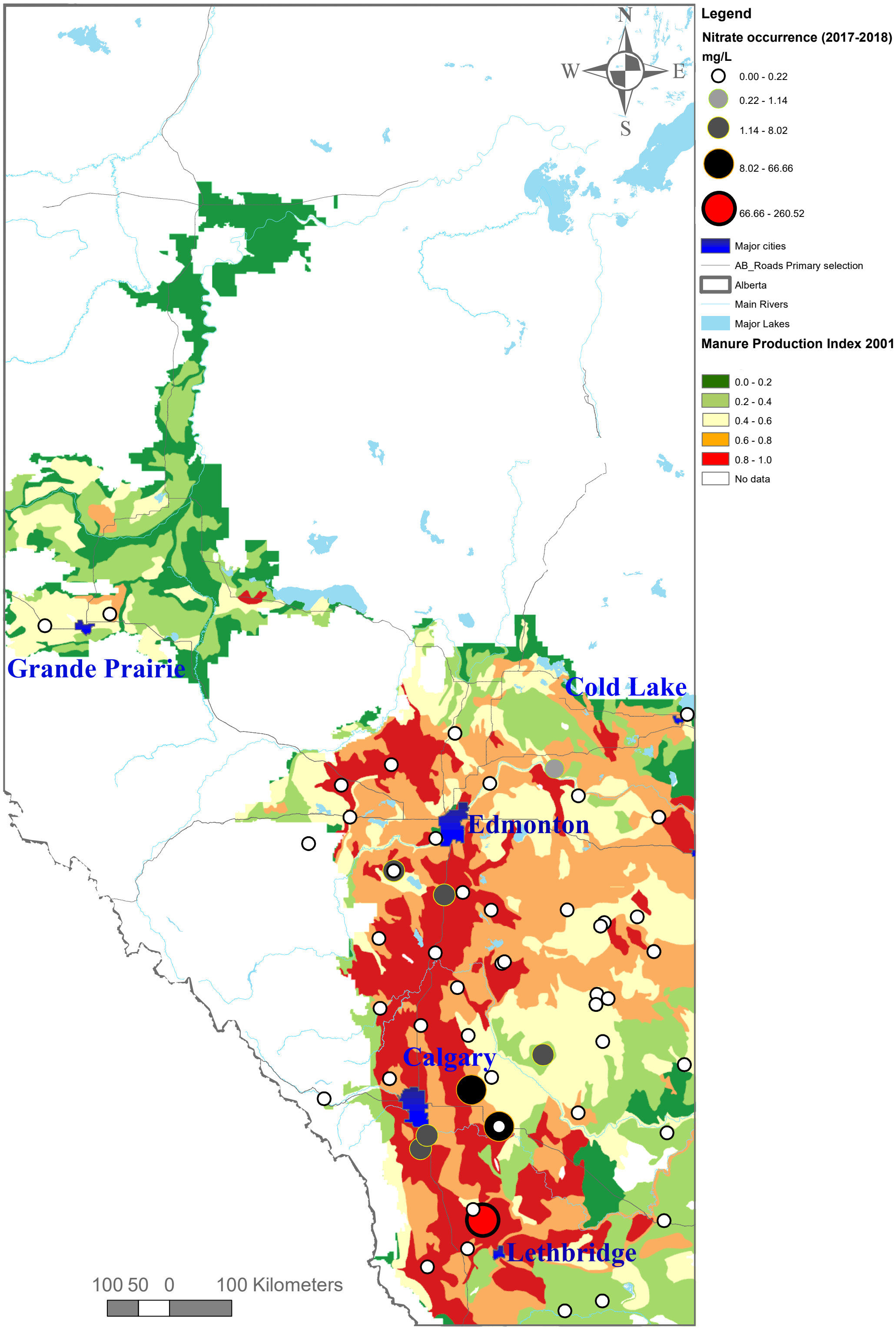

***Figure 8b:** Occurrence of nitrate in groundwater samples, southern Alberta from GOWN wells. Under layer displays the relative amount of manure production in the agricultural area. The classes shown on the map were ranked from 0 (lowest risk) to 1 (highest risk) (from Alberta Agriculture and Forestry, Government of Alberta, layer created in 2002).*

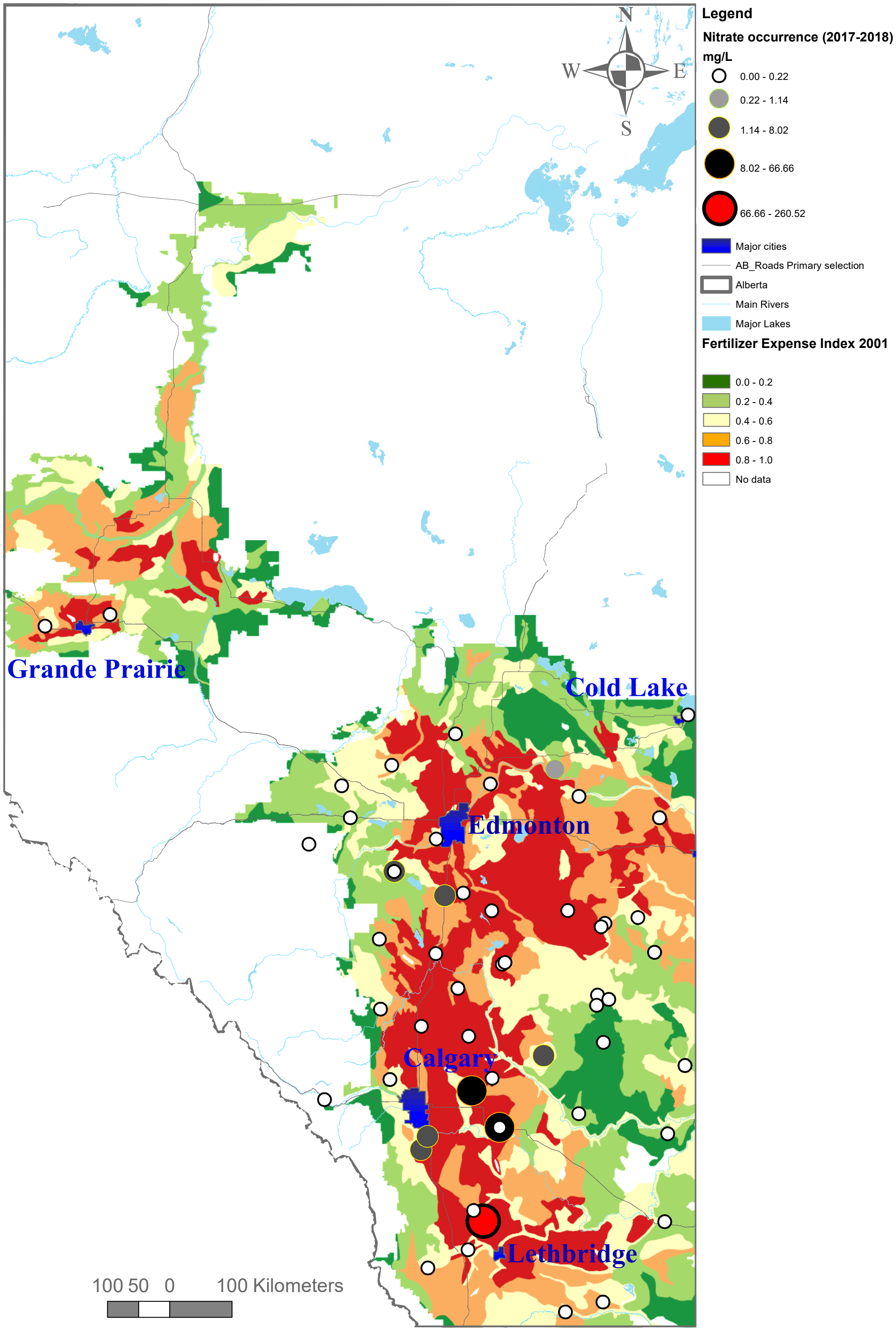

Figure 8c: *Occurrence of nitrate in groundwater samples, southern Alberta collected from GOWN wells. Under layer displays the relative expense of fertilizer in the agricultural area. The classes shown on the map were ranked from 0 (lowest risk) to 1 (highest risk) (from Alberta Agriculture and Forestry, Government of Alberta, layer created in 2002).*

5.4.1.2 Processes removing nitrate from groundwater

More than 87% of the GOWN groundwater samples had no nitrate. In Figure 9a, there was a trend of groundwater samples with low nitrate concentrations (e.g. <2 mg/L) having elevated δ^{15}N values of +20‰ and more. This is an indication that denitrification has occurred, a process during which nitrate is reduced to harmless N_2, while ^{15}N becomes enriched in ^{15}N as nitrate concentrations decrease with nitrogen isotope enrichment factors ranging from -2 to -30 ‰ (Wada et al., 1975; Vogel et al., 1981). These interpretations are confirmed in Fig. 9b that shows a group of samples with δ^{15}N values between +2 and +8 ‰ and δ^{18}O values < -5 ‰ suggesting a mixture of nitrate derived from manure and synthetic fertilizers inputs after significant N recycling in the agricultural soils. A second group of samples plots along a trend-line with a slope of 0.4 (r^2 =0.6) of increasing δ^{15}N and δ^{18}O values of nitrate. This is an indication that these samples have undergone partial denitrification, a process during which the remaining nitrate becomes enriched in ^{15}N and ^{18}O as nitrate concentrations decrease.

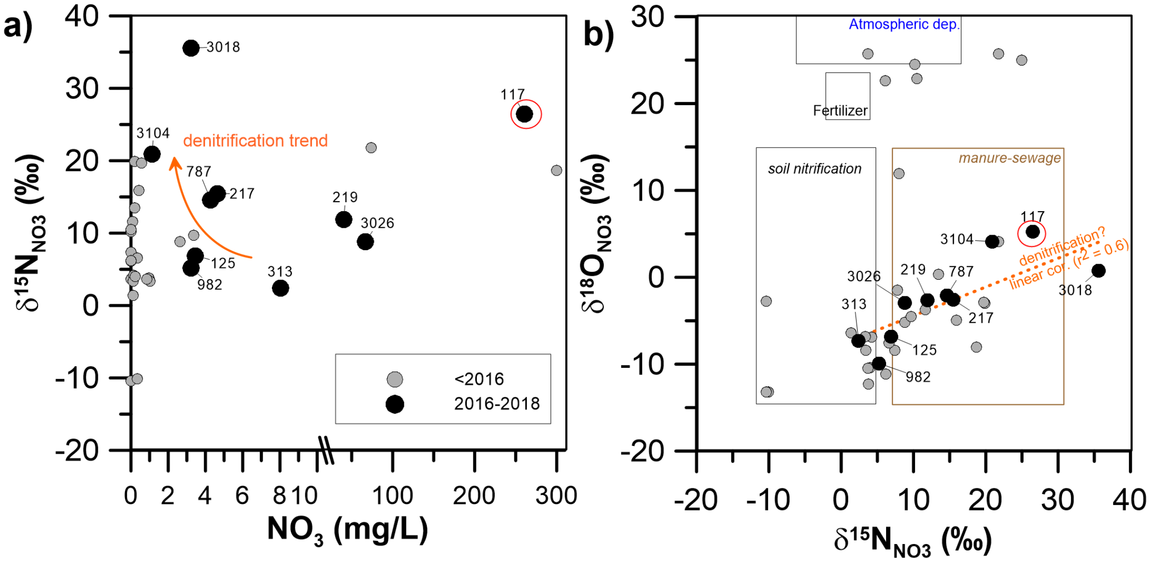

Figure 9: *a) Nitrate concentration versus $\delta^{15}N_{NO3}$ in groundwater samples b) $\delta^{18}O_{NO3}$ versus $\delta^{15}N_{NO3}$ values of groundwater nitrate.*

To determine the relation between concentrations and δ^{15}N values in the remaining nitrate after partial denitrification, the measured δ^{15}N values were evaluated using a Rayleigh equation as follow:

$$\delta^{15}_{NO3,r} = \delta^{15}_{NO3,0} + \varepsilon \cdot \ln f \quad \text{(Eq. 1)}$$

with $\delta^{15}_{NO3,r}$ the delta value (‰) of the residual nitrate after denitrification, $\delta^{15}_{NO3,0}$ the delta value (‰) of the initial nitrate before the denitrification process starts, ε the isotopic enrichment factor (‰) and f the fraction between the concentration of the remaining and initial nitrate.

$$f = \frac{NO_3}{NO_{3,0}} \quad \text{(Eq. 2)}$$

Two different initial nitrate concentrations were tested with 25 mg NO_3^--N/L (source A) and 100 mg NO_3^--N/L (sources B and C). The $\delta^{15}_{NO3,0}$ value of +2‰ was chosen for sources A, and B indicative of nitrification of soil organic matter or ammonium- and urea-based synthetic fertilizers. For source C a $\delta^{15}_{NO3,0}$ value of +10‰ was selected indicative of manure-derived nitrate. N isotope enrichment factors varied from -5 to -25‰. Figure 10a reveals that the majority of the samples plotted on the diagram have undergone partial denitrification. Figure 10b reveals that this process occurs with a variety of different initial nitrate concentrations and nitrogen isotope enrichment factors, making the quantification of the extent of denitrification somewhat challenging.

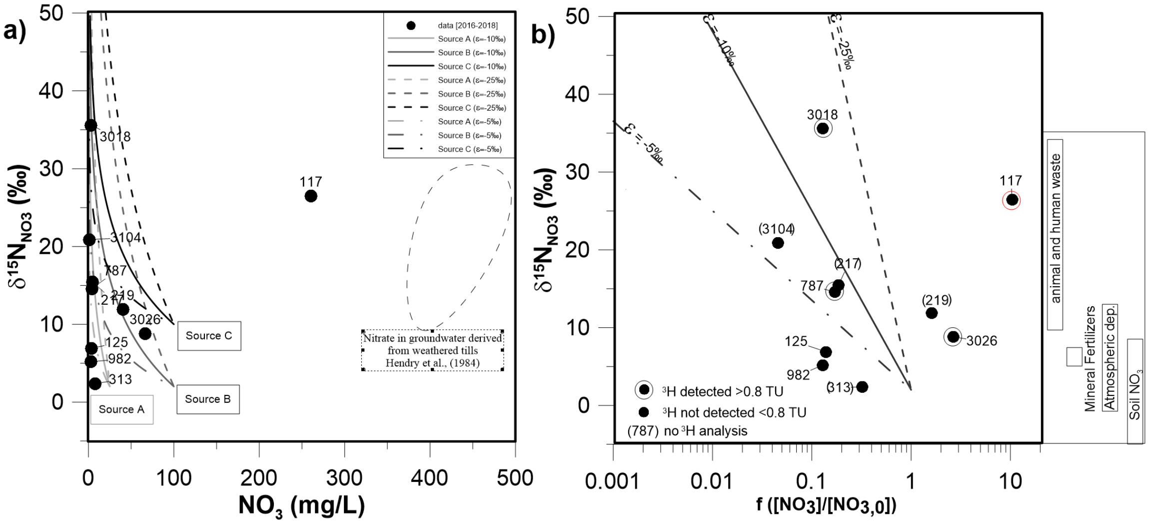

Figure 10: *Relationships between N isotope ratios in the remaining nitrate with a) its concentration and b) the fraction of the f of he remaining nitrate (logarithmic scale) during the denitrification process. Note: tritium analyses results are shown in plot b.*

Groundwater sample #117 is unique since it has very high nitrate concentrations and $\delta^{15}N$ values. The groundwater well from which this sample was collected is located near Lethbridge in the Oldman River watershed (Fig. 2), and area characterized by intensive agriculture (Figs. 2a-c), and the sample was produced from the Horseshoe Canyon formation. The nitrate concentrations of groundwater obtained from this well between 2007 and 2018 varied between 260 and 329 mg NO_3^--N/L (n=4). Isotope analyses revealed that this nitrate has $\delta^{15}N$ value of +26.5 ‰ and a $\delta^{18}O$ value of +5.3 ‰. The groundwater is also characterized by a very high TDS value of >14,000 mg/L very high concentrations of sulfate (>9,500 mg/L), magnesium (>360 mg/L), and sodium (>4,000 mg/L), while a tritium content of 8.7 TU revealed that some of the groundwater is less than 50 years old. While this very unique geochemical and isotopic composition requires further investigation, it is possible that this nitrate is derived from geogenic sources. Weathering of glacial till in southern Alberta can result in nitrification of ammonium released from clays upon weathering of the clay lattice, in in-situ mineralization and subsequent nitrification of organic nitrogen within the till, conversion of organic nitrogen to nitrate due to presence of oxygen, and nitrification of exchangeable ammonium (Hendry et al., 1984). The tritium content of 9 TU in the groundwater suggest some freshly recharged water saturated with oxygen that could accelerate the nitrification processes, while the isotopic composition of sulfate ($\delta^{34}S_{SO4}$ +1.3‰, $\delta^{18}O_{SO4}$ -15.1‰)

indicates that pyrite oxidation occurred. Alternately, it should be tested whether the elevated concentrations of nitrate are caused by anthropogenic sources such as manure, but the extraordinarily high $\delta^{15}N$ values in concert with the very high nitrate concentrations raise some doubts that manure-derived nitrate is the dominant source affecting this groundwater.

The obtained results reveal that only a small subset of GOWN groundwater samples contains elevated nitrate concentrations. Furthermore, it was shown that many of these samples are affected by partial denitrification, a process that converts the groundwater contaminant nitrate into harmless N_2. This supports previous findings that redox conditions for persistence of nitrate in groundwater are only favourable in shallow and young groundwater. In contrast, the more reducing conditions of geochemically evolved, older, and deeper groundwater are not suitable for the occurrence of nitrate.

5.4.2 Sources and fate of methane

To determine the sources of methane in groundwater obtained from GOWN wells, gas compositions and carbon isotope ratios of methane in dissolved gas samples (n_{conc} = 246; n_{iso}=161) and free gas samples (n_{conc} = 137; n_{iso}=121) were determined and results are shown in Fig. 5. The results indicate that there is a strong correlation and excellent agreement between the concentrations (Fig. 5a) and carbon isotope ratios of methane (Fig. 5b) in free and dissolved gas samples with only few exceptions. The excellent agreement between results from free gas and dissolved gas samples is consistent with Henry's law and demonstrates that the sampling and analytical approaches are highly reliable and accurate.

Figure 5c provides a cross-plot of the concentrations versus the carbon isotope ratios of methane. The majority of the samples (>65%) had $\delta^{13}C\text{-}CH_4$ values of less than -58 ‰, indicating that this methane is of biogenic origin (e.g. methane is produced by micro-organisms at low temperatures). Circa 34% of the samples had $\delta^{13}C\text{-}CH_4 > -55$ ‰, but almost all of these samples were associated with very low methane concentrations (Fig. 5c, black area). This is indicative of oxidation of biogenic methane. During this process, methane is partially converted to CO_2, while the remaining methane becomes progressively enriched in ^{13}C resulting in increasing $\delta^{13}C$ values of methane. The occurrence of this process in shallow aquifers often results in so-called pseudo-thermogenic carbon isotope fingerprints of the remaining methane that can be easily misinterpreted as an intrusion of thermogenic methane derived from deep (> 1 km) sedimentary layers and reservoirs. It is often very challenging to differentiate between methane from deep thermogenic sources and biogenic methane that has undergone partial oxidation in shallow aquifers solely based on concentration and isotope measurements of methane.

To address this critically important ambiguity in accurately identifying the occurrence of thermogenic methane in shallow groundwater, we have developed a combined geochemical and multi-isotope model that considers in addition to the isotopic composition of methane also the concentrations and isotopic compositions of dissolved inorganic carbon (DIC) and sulfate (Humez et al., 2019). The additional aqueous parameters considered in this model enable us to determine whether methane oxidation has occurred either under aerobic conditions, or anaerobically coupled with denitrification or bacterial sulphate reduction (BSR). Furthermore, this model enables the calculations of the isotopic composition of methane that has been partially oxidized, and hence facilitates source identification of methane.

Table 1: Subdivision of groundwater samples obtained from GOWN wells in five different categories based on a novel modeling approach considering the chemical compositions of methane, DIC and sulfate (from Humez et al., 2019).

Category	Description	SO_4 conc.		CH_4 conc		$\delta^{13}C_{CH4}$		$\delta^{13}C_{DIC}$		Well
		>1 mM	<1 mM	> 0.01mM	< 0.01mM	> –55‰	< –55‰	> +0‰	<–10 ‰	
1a	Intrusion of microbial methane into a sulfate-rich groundwater zone; methane oxidation coupled with bacterial sulphate reduction (BSR) is a key processes	■			■	■			■	114,148,229, 234,381,398, 481
1b	Same as category 1, but with higher methane concentration variability	■			■	■			■	126,144, 373
2	Intrusion of microbial methane into a sulfate-poor groundwater zone; the low initial sulfate concentration was originally caused by bacterial sulphate reduction		■	■			■		■	438, 439, 982
3	Intrusion of microbial methane into a sulfate-poor groundwater zone. The sulfur isotope ratios of sulfate indicate only minor BSR, suggesting that the initial water did not have high sulfate concentrations		■	■			■		■	456
4	Advanced methanogenesis in a groundwater showing little evidence of BSR, indicating an initially sulfate-poor groundwater		■	■		■	■	■		214,310/311, 333, 991
5	Groundwater with low concentrations of sulfate and methane		■		■				■	140, 984

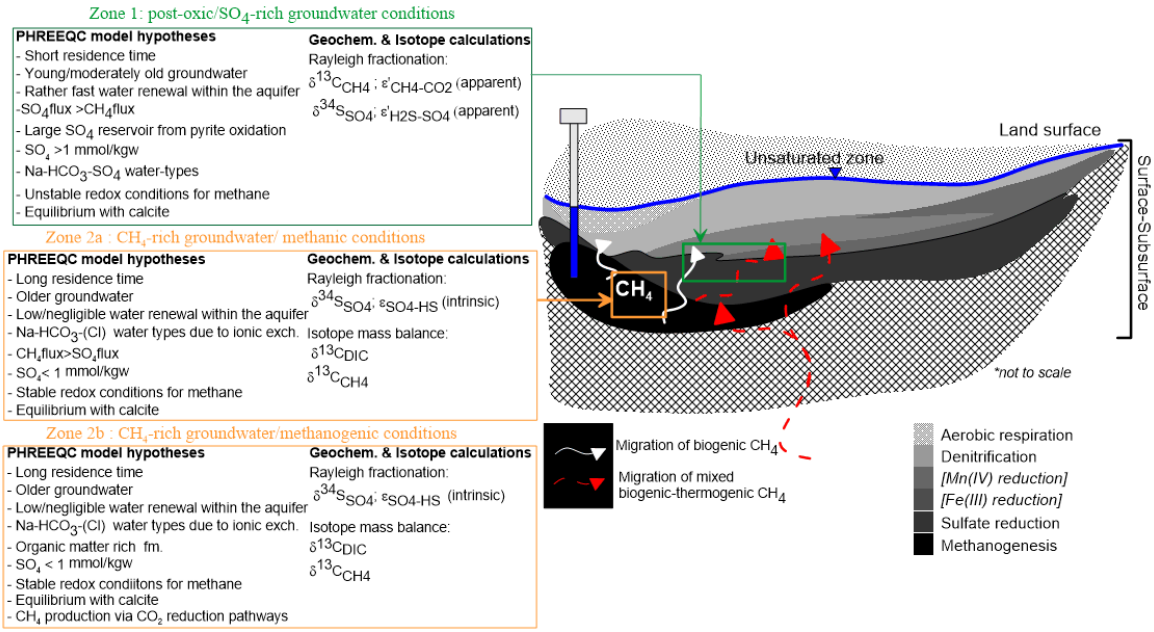

Figure 11: *Subdivision of groundwater samples obtained from GOWN wells based on their geochemical and isotopic compositions and a novel PHREEQC model developed during this study (from Humez et al., 2019).*

Application of this model revealed no contamination of aquifers accessed by GOWN wells by deep thermogenic methane. In all cases, methane was found to be of biogenic origin (Fig. 5c), or methane of biogenic origin was partially oxidized coupled with bacterial sulfate reduction (BSR). Table 1 and Figure 11 details the various redox zones in which methane is either formed in-situ in the shallow aquifers, or has been partially oxidized.

5.5 Project outcomes and important lessons learned

The combination of geochemical and isotopic techniques combined with groundwater dating and geochemical modeling approaches enabled the research team to classify the groundwater samples obtained from GOWN wells into 3 different categories:

Type I: Modern groundwater of Ca-HCO_3 type containing tritium containing little to no methane
This category contains modern groundwater with $^3H > 0.8$ TU that dominated by Ca^{2+} and HCO_3^- with either no methane or low to negligible methane concentrations (median value of $3.8 \bullet 10^{-4}$ mmol/L) and has low median TDS contents of 306 mg/L (Table 2; Fig. 12). This modern groundwater has $F^{14}C_{DIC}$ values varying from 40 to 89 % modern carbon similar to the young groundwater from Vogel (1970) of 85±5 % modern carbon. The redox conditions are not reducing enough and favorable for methane to be either produced or persist due to elevated concentrations of nitrate and sulfate. Therefore, samples with low concentrations of methane reveal evidence of methane oxidation coupled with bacterial sulfate reduction or denitrification. In consequence, $\delta^{13}C_{CH4}$ values in these groundwater samples vary from -61‰ to -22 ‰, while $\delta^{13}C_{DIC}$ values near -12‰ are indicative of carbonate dissolution.

Type II: Geochemically more evolved groundwater of Na-HCO_3 type, without tritium and with moderate methane concentrations
This category contains groundwater that is more than 50 years old with water types that have evolved from Ca-HCO_3 to Na-HCO_3. A decrease in sulfate concentrations and moderate methane concentration indicate a more reducing groundwater environment facilitating the occurrence of methane with a median concentration of $1.2 \bullet 10^{-2}$ mM and a median $\delta^{13}C$ value of -69.4‰. Elevated $\delta^{34}S_{SO4}$ values range between 0 and +25‰ suggesting the occurrence of bacterial sulfate reduction confirming a reducing groundwater environment. $F^{14}C_{DIC}$ values ranging from <0.5 (detection limit) to 40 % modern carbon indicate that this groundwater is considerably older than that of category I. Methane oxidation coupled with bacterial sulfate reduction as well as carbonate dissolution are likely water-gas-rock interaction processes in this groundwater system controlling the isotope and geochemical compositions of the obtained groundwater samples.

Type III: Geochemical mature groundwater of Na-(HCO_3)-Cl type without tritium, with elevated methane concentrations, and ^{14}C contents below the detection limit
This category contains groundwater that is geochemically very mature with Na^+ and Cl^- dominating the water type. These samples are characterized by elevated methane concentrations with a median value of 3.1 mM and $\delta^{13}C_{CH4}$ values < -71.3‰, indicative of biogenic methane. $\delta^{13}C_{DIC}$ values > 0‰ provide evidence that methanogenesis occurs in-situ in these aquifers. These groundwater samples collected from

aquifers with organic rich sediments such as the Horseshoe Canyon, Belly River, and Bearspaw Formations contain no tritium and ^{14}C activities were consistently below the detection limit of the radiocarbon technique (see Table 2, Fig. 12) suggesting considerable groundwater ages of hundreds to thousands of years.

Table 2: Classification of groundwater samples in three different categories

Key-contaminant	Water well depth	Hydrochemical facies	Redox condition	Age dating data	Processes
Elevated methane conc.	X	$Na-(HCO_3)-Cl$ $Na-HCO_3$	Anoxia Low NO_3 Low SO_4	Low to below detection $F^{14}C_{DIC}$ No ^3H detected ⇔ Older groundwater	**Methanogenesis** evidenced by $\delta^{13}C_{CH4}$, $\delta^{13}C_{DIC}$,
Low methane conc.	X	$Ca-Mg-HCO_3$ $Na-SO_4$	Elevated SO_4/NO_3 conc.	Higher $F^{14}C_{DIC}$ ^3H detected ⇔ Younger groundwater	**Methane oxidation** coupled with **sulfate reduction** evidenced by $\delta^{13}C_{CH4}$, $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$
Elevated nitrate conc.	Shallow horizons	$Na-SO_4$ $Ca-Mg-HCO_3$	Elevated SO_4 Low to negligible CH_4	Higher $F^{14}C_{DIC}$ ^3H detected ⇔ Younger groundwater	Ongoing **denitrification** processes evidenced by $\delta^{15}N_{NO3}$

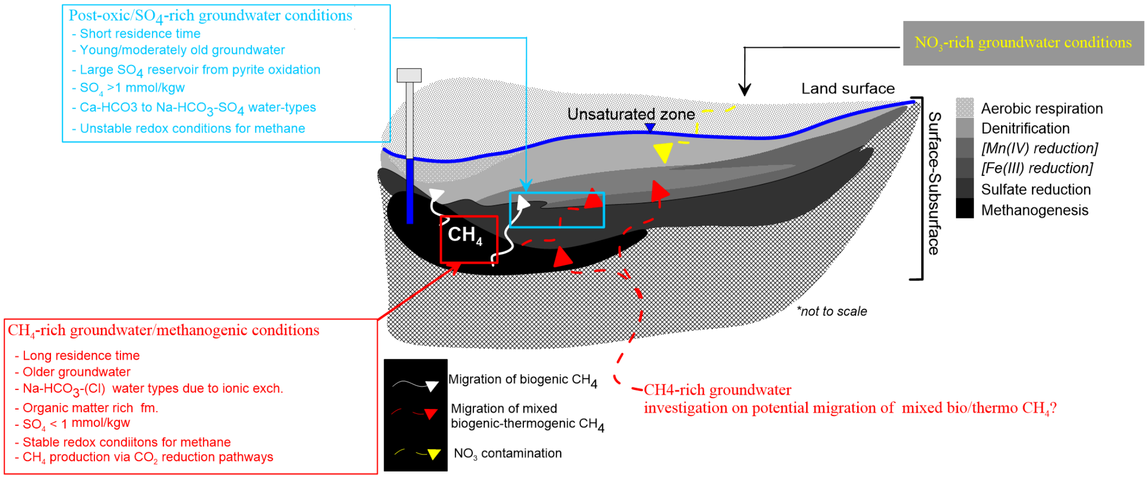

Figure 12: *Classification of groundwater samples in three different categories.*

The application of geochemical and isotopic techniques combined with groundwater dating and geochemical modeling approaches revealed a systematic evolution that progresses from young, oxidizing Ca-HCO_3 type groundwater in shallow aquifers, which may contain elevated concentrations of nitrate but has no or only negligible contents of methane, towards a more geochemically evolved and much older Na-HCO_3 to Na-(HCO_3)-Cl type groundwater in deeper aquifers. This groundwater contains typically no nitrate, but often has elevated concentrations of methane that is of biogenic origin.

6. Relevance and Impact

Environmental benefits

The research program yielded a much-improved understanding about the quality of groundwater in Alberta accessed through GOWN wells. The newly obtained knowledge will result in considerable environmental benefits for those Albertan's who depend on groundwater for drinking water purposes. The obtained findings are highly relevant to Alberta's Water Research and Innovation Strategy goals "Reliable, Quality Water Supplies for a Sustainable Economy" and "Safe Secure Drinking Water" and to the Groundwater Management Frameworks under the land-use framework planning. Our research team has applied innovative geochemistry-based approaches that improved the previously incomplete understanding of the processes that impact the quality and sustainability of groundwater resources on which many Albertans depend. Specific environmental benefits of the conducted research program relate to: 1) **Groundwater Quality** due to a much improved understanding of the sources of contaminants such as nitrate and methane, and biogeochemical reactions such as denitrification and methanogenesis, that impact and control groundwater quality in Alberta; **2) Groundwater Sustainability** due to first attempts to map groundwater age distributions and dissolved groundwater parameters including the extent of contamination with nitrate and methane in dependence of groundwater age.

Economic benefits

Understanding the quality of groundwater and the timelines at which contaminants reach groundwater or are biodegraded in aquifers provides tremendous economic benefits for the province of Alberta. One key deliverable of the project was that it identified the extent of nitrate pollution in young, shallow groundwater, while high-quality groundwater supplies were identified in areas where surface water supplies are increasingly constrained or over-allocated. Providing safe and secure drinking water from aquifers for a growing population and supplying quality water for a growing economy has tremendous benefits for the province, although this benefit is difficult to quantify.

Another major benefit derived from this project is due to its beneficial impact on future sustainable extraction of unconventional oil and gas resources in Alberta. Development of natural gas and associated condensates from unconventional hydrocarbon resources is an important economic driver for the province and its energy systems. There is, however, the fear in some parts of the public that hydraulic fracturing may have a detrimental impact on the quality of our shallow groundwater resources and that leakage of fracturing fluids or of stray gases may negatively impact the quality of our aquifers. To test in a scientifically sound manner whether such impacts on the quality of groundwater do occur, it is essential to have solid baseline data on the quality of groundwater in Alberta and its associated gases. This project provided province-wide information on the occurrence of methane and ethane and its sources in aquifers accessed by GOWN wells. This information provides an unprecedented baseline against which future impacts on shallow groundwater by the oil and gas industry, or the lack thereof, can be scientifically assessed. Therefore, this project will make a critically important contribution to address public concerns with respect to hydraulic fracturing and will help the oil and gas industry with maintaining their social license to operate.

Societal benefits

Our research team has improved the previously incomplete understanding of the processes that impact the quality and sustainability of groundwater resources on which many Albertans already depend for drinking water and for sustaining food and energy supplies. Hence the societal benefits of the findings from this study are mainly linked to an improved supply of safe and secure drinking water from aquifers for a growing population with the goal to provide quality water for a growing economy. This will have considerable benefits for the province in future years.

Building Innovation Capacity

Integral to this project was the training of highly skilled personnel (HSP), including one MSc student, one postdoctoral fellow, and several research associates. Through training in this project, the HSP obtained skills that are highly sought after by regulators, governments, industry and academia alike. All these trainees were either retained as employees at the University of Calgary or found employment in the oil and gas sector of Alberta.

7. Overall Conclusions

The research team conducted an in-depth analysis and interpretation of the aqueous geochemistry, the stable isotopic compositions of water and dissolved constituents, and the groundwater ages for samples obtained from selected Groundwater Observation Well Network (GOWN) wells in Alberta. The unique stable isotope results yielded novel information about sources of water and its dissolved methane, ethane, nitrate, carbon and sulfate in shallow groundwater of Alberta, and revealed whether gases such as methane had formed in-situ in these freshwater systems or had migrated into the aquifers from below. The project also combined chemical, isotopic, and groundwater dating results to assess variations in groundwater types and redox states, while the use of groundwater dating tools yielded information about age distribution of shallow groundwater in Alberta to quantify timespans required for select contaminants (e.g. methane, nitrate) to build up or degrade.

The application of geochemical and isotopic techniques combined with groundwater dating approaches revealed a systematic evolution that progresses from young, oxidizing Ca-HCO_3 type groundwater in shallow aquifers, which may contain elevated concentrations of nitrate but has at most negligible amounts of methane, towards a more geochemically evolved and much older Na-HCO_3 to Na-(HCO_3)-Cl type groundwater in deeper aquifers. This groundwater contains typically no nitrate but often has elevated concentrations of methane that is of biogenic origin. Hence the project confirmed all three initial hypotheses, namely that:

4. Younger groundwater is generally more oxidizing, whereas older groundwater was found to be highly reducing;
5. Nitrate contamination was detected predominantly in young and shallow groundwater; in contrast elevated methane contents were restricted to deeper and much older groundwater units;
6. There exists an intermediate zone where the reduction of nitrate and sulfate may be coupled to the oxidation of methane.

The project yielded also very low-resolution maps for selected groundwater pollutants such as nitrate, and has clearly demonstrated the tremendous potential of this approach in case that larger regional groundwater data sources can be accessed.

8. Next Steps

This project was restricted to high quality groundwater samples from only 90 GOWN wells throughout the province of Alberta. The logical next step is to conduct a much more expanded investigation in determining the occurrence, origin and fate of aqueous contaminants in Alberta groundwater by using other existing aqueous geochemistry data sets such as the Baseline Well Water Testing (BWWT) database and the groundwater quality data housed in Alberta Health Services (AHS). The four key reasons for such a project extension are: 1) This new research effort would expand the previous work of investigating groundwater contamination from 90 GOWN well sampling sites to more than 80,000 groundwater observation points (constituting an 890-fold increase of resolution) by including water quality data from Alberta's Baseline Water Well Testing (BWWT) program (>15,000 samples) and the Alberta Health Services (AHS) groundwater database (>65,000 samples) in its analysis. Including information from GOWN, BWWT and AHS data sources would enable for the first time a truly high-resolution, province-wide assessment and characterization of groundwater contamination in the province of Alberta. 2) This expanded work would investigate the origin and potential fate of dissolved constituents including manganese, iron, selenium, fluoride and radon, among others: these are potential contaminants that were not included in previous projects. 3) Furthermore, it is recommended to use highly innovative metagenomics approaches to provide information about bacterial presence and activity in groundwater to reveal how these naturally occurring microbial communities influence groundwater quality and the fate of contaminants in Alberta's aquifers. 4) Through the use of subsurface information from the Alberta Water Well Information database (AWWID) and the Alberta Geological Survey (AGS), it would be possible for the first time to incorporate high-resolution groundwater quality and contamination data into a 3D aquifer framework to understand the relationship of water contaminants with well depths, aquifer units, and hydrostratigraphic delineation (e.g. geological formation). This multi-pronged innovative approach would yield a better understanding of the province-wide occurrence, origin and fate of select groundwater contaminants and an enhanced delineation of aquifers. Together these results would provide an unprecedented knowledge of the groundwater quality conditions for water users in Alberta.

9. Communications plan

The research project was conducted in close collaboration with scientists in the Environmental Monitoring and Science Division (EMSD) of Alberta Environment and Parks (AEP). Dr. Cynthia McClain was actively involved in planning the fieldwork, was regularly briefed about the obtained results, and is fully aware of the key findings of this project. In addition, she played an important role in co-supervising and mentoring the MSc student and the postdoctoral fellow in this project.

The project results have also been communicated to Dan Palombi and Dr. Brian Smerdon at the Alberta Geological Survey (AGS) to inform Alberta's groundwater programs including the Provincial Groundwater Inventory Program (PGIP). The shared information will help to support water policy and regional planning initiatives in the province, including environmental management frameworks.

Project results were regularly presented at Alberta Innovates Water Innovation Program workshops and conferences. Furthermore, select project results have been communicated to the scientific community via presentations at conferences and symposia and through peer-reviewed publications in international peer-reviewed journals.

10. Scientific Achievements

Journal articles published or in press:

Humez, P., Osselin, F., Kloppmann, W. & Mayer, B. (2019): A geochemical and multi-isotope modeling approach to determine sources and fate of methane in shallow groundwater above unconventional hydrocarbon reservoirs. - Journal of Contaminant Hydrology, accepted July 19, 2019.

Jasechko, S., Wassenaar, L. I. & Mayer, B. (2017): Isotopic evidence for widespread cold-season-biased groundwater recharge and young streamflow across central Canada. - Hydrological Processes, 31 (12) 2196-2209. Doi: 10.1002/hyp.11175

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Students and other personnel trained:

Leah Wilson, MSc student, Shallow groundwater quality in Alberta with focus on the occurrence of nitrate and methane. MSc thesis completed and defended in April 2019.

Dr. Pauline Humez, Postdoctoral fellow throughout the project duration, Department of Geoscience, University of Calgary.

Conference presentations:

12 presentations at provincial, national and international meetings, symposia and conferences.

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