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## Prospects and limitations of chemical and isotopic groundwater monitoring to assess the potential environmental impacts of unconventional oil and gas development

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### Abstract

With the advent of shale oil and shale gas development facilitated by hydraulic fracturing it has become increasingly important to develop tracer tools to scientifically determine potential impacts of stray gases, formation fluids, or fracturing chemicals on shallow aquifers. Based on a multi-year monitoring program conducted in Alberta (Canada), we demonstrate that a multi-isotope approach ( $\delta^2\text{H}_{\text{H}_2\text{O}}$ ;  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ ;  $\delta^{13}\text{C}_{\text{CH}_4}$ ;  $\delta^2\text{H}_{\text{CH}_4}$ ;  $\delta^{13}\text{C}_{\text{C}_2\text{H}_6}$ ) in concert with chemical analyses is highly capable of identifying potential contamination of shallow aquifers with stray gases or saline fluids from intermediate or production zones, provided that sufficient baseline data have been collected. At baseline conditions, we found that methane in shallow groundwater in southern Alberta is ubiquitous and predominantly of biogenic origin. Novel approaches of in-situ concentration and isotope measurements for methane during drilling of a 530 m deep well yielded a mud-gas profile characterizing natural gas occurrences in the intermediate zone. The assembled data set provides evidence that potential stray gas contamination by isotopically distinct deeper thermogenic gases from the intermediate or from production zones can be effectively detected by suitable monitoring programs.

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## 1. Introduction

Natural gas extraction from unconventional resources such as shale is currently transforming the global energy outlook. The recent expansion of the unconventional gas industry in North America and the planned advent of this technology in parts of Europe have, however, generated public concern regarding the potential contamination of shallow groundwater and surface waters by natural gas and by hydraulic fracturing flow-back fluids containing saline formation waters together with fracturing chemicals. Currently, there is often a paucity of reliable scientific data on extents and rates of leakage of stray gases and reservoir fluids in the vicinity of shale gas wells<sup>1</sup>.

A major challenge for environmental impact assessment in the context of unconventional petroleum exploitation is the determination of the non-impacted baseline conditions often termed environmental baseline assessment. Groundwater and surface water resources overlying the low-permeability host rocks of shale oil and gas may be impacted to different extents by naturally occurring saline fluids and by natural gas emanations<sup>2</sup>. Therefore, it is of key importance to determine chemical and isotopic compositions of water, dissolved constituents, and dissolved or free gases including methane in surface waters and shallow aquifers, in the intermediate zone below the base of groundwater protection, and in the formations from which unconventional energy resources are extracted.

The study objective was to evaluate prospects and limitations of chemical and isotopic monitoring approaches in shallow aquifers, the intermediate zone and producing formations to assess the potential environmental impacts of unconventional oil and gas development with specific emphasis on methane in fugitive gas.

## 2. Sampling & Methods

Carbon Management Canada Research Institutes Inc. (CMC) is constructing a Field Research Station (FRS) to develop, demonstrate and calibrate various surface and subsurface monitoring technologies for stray gas detection, among others. CMC has recently completed a 530 m deep research well at the FRS approximately 20 km southwest of Brooks (Alberta, Canada) on land donated by Cenovus Energy. During the drilling in winter 2015, mud-gases (gases released from the drilling fluids captured at the mud shaker at the drilling rig) were collected continuously at the well site (Fig. 1a) and concentrations and  $\delta^{13}\text{C}$  values of methane were determined in the field (Fig. 1b) using cavity ring-down laser absorption spectroscopy (Picarro 2201-i) with a measurement uncertainty of 0.55 ‰.

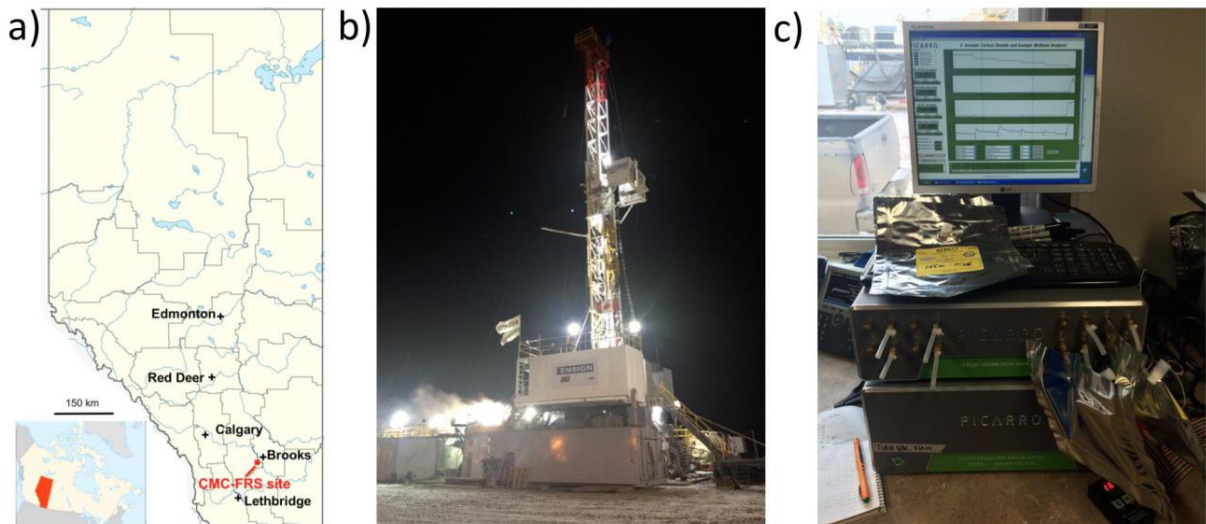


Fig. 1. a) Location of the Carbon Management Canada Research Institutes Inc. (CMC) Field Research Station (FRS) near Brooks (Alberta, Canada), b) drilling of well Countess 10-22-17-16W4 in Newell county near Brooks, and c) measurement of concentrations and  $\delta^{13}\text{C}$  values of methane in mud-gases at the site using cavity ring-down laser absorption spectroscopy.

Groundwater was sampled from more than 40 monitoring wells of the Alberta Groundwater Observation Well Network (GOWN) within a 150 km radius of the CMC FRS (Fig. 2a) and water quality parameters were analysed using standard approaches. The isotopic composition of groundwater ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) was determined using a Los Gatos Research ‘DLT-100’ laser spectroscopy instrument. Free gas and dissolved gas samples were obtained and concentrations of methane, ethane,  $\text{N}_2$  and  $\text{CO}_2$  were determined by gas chromatography. The  $^{13}\text{C}/^{12}\text{C}$  and  $^2\text{H}/^1\text{H}$  ratios of methane and ethane (where possible) were analyzed by isotope ratio mass spectrometry (IRMS) coupled to GC combustion and pyrolysis with precisions of  $< \pm 0.5\text{‰}$  and  $< \pm 3\text{‰}$ , respectively.

### 3. Results & Discussion

The obtained shallow groundwater samples were predominantly of  $\text{Na-HCO}_3^-$  type with total dissolved solids (TDS) ranging from  $< 800$  mg/L to  $> 1800$  mg/L. The  $\delta^{18}\text{O}$  values of groundwater varied from  $-15.0$  to  $-22.0$  ‰ with an average of  $-19.0$  ‰ and the  $\delta^2\text{H}$  values varied from  $-125$  to  $-174$  ‰ with an average of  $-149$  ‰ (data not shown). These values are consistent with the average  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of precipitation in southern Alberta and plot close to the local meteoric water line<sup>3</sup> indicating that groundwater is of meteoric origin and recharges with only minor impact from evaporation.

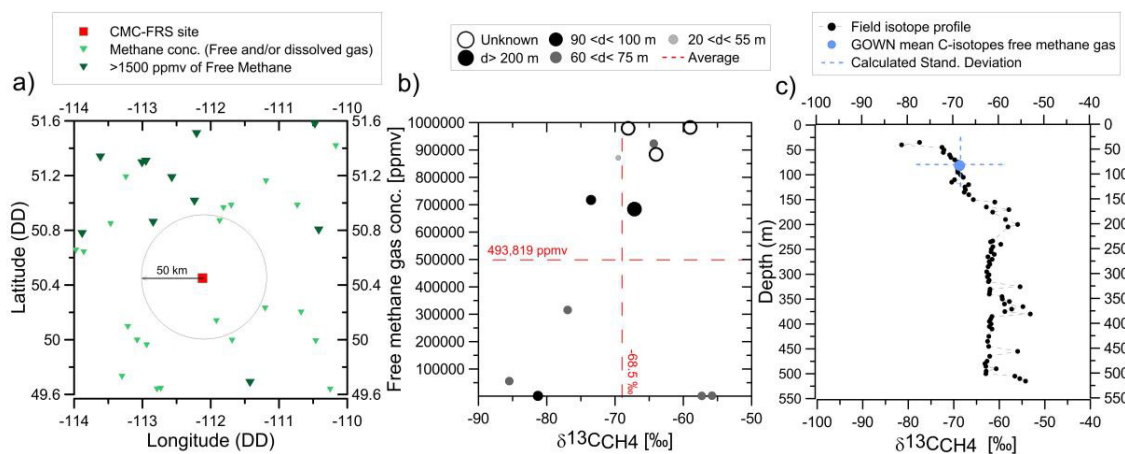


Fig. 2. a) Location of 40 GOWN wells sampled for groundwater and free and dissolved gas; b) methane concentrations versus  $\delta^{13}\text{C}$  values of methane in free gas from selected GOWN wells; c)  $\delta^{13}\text{C}$  of methane for mud-gas depth profile for well Countess 10-22-17-16W4 at the FRS.

Figure 2b reveals that methane concentrations in free gas samples from groundwater wells varied from  $< 1,500$  ppmv to  $> 980,000$  ppmv with the highest methane concentrations observed in groundwater monitoring wells completed in the coal-rich Horseshoe Canyon Formation.  $\delta^{13}\text{C}$  values of methane varied from  $-86$  to  $-55$  ‰ yielding an average  $\delta^{13}\text{C}$  value of  $-68.5$  ‰. These negative  $\delta^{13}\text{C}$  values in concert with  $\delta^2\text{H}$  values of methane near  $-302$  ‰ indicate that the methane occurring in shallow groundwater in the study area is of biogenic origin<sup>4</sup>.

Figure 2c displays a depth profile of  $\delta^{13}\text{C}$  values of methane from mud-gas analysis throughout the Upper Cretaceous sedimentary succession accessed by well Countess 10-22-17-16W4. Methane in the uppermost section of the well ( $< 50$  m) has the lowest  $\delta^{13}\text{C}$  values around  $-80$  ‰. With increasing depth towards 150 m below ground surface,  $\delta^{13}\text{C}$  values of mud-gas methane increased to  $-62$  ‰. With further increasing depth, the  $\delta^{13}\text{C}$  values of mud-gas methane remained constant at  $-62$  ‰ with the exception of several excursions to  $\delta^{13}\text{C}$  values as high as  $-54$  ‰ suggesting increasing contributions of either secondary biogenic gas derived from biodegradation of oils<sup>5</sup> or of thermogenic gas with increasing depth<sup>6</sup>.

In Figure 2c, the average  $\delta^{13}\text{C}$  value of methane in groundwater is plotted at the average groundwater well depth of  $\sim 80$  m on top of the mud-gas  $\delta^{13}\text{C}$  profile generated by cavity ring-down laser absorption spectroscopy for well Countess 10-22-17-16W4. The excellent agreement of the average carbon isotope ratio of methane in free gas of groundwater with the mud-gas results suggests that methane observed in shallow groundwater in the wider vicinity

of the CMC Field Research Station was generated predominantly biogenically in the shallow portion of the sedimentary column, with little indication of migration of very deep thermogenic gases into the near-surface environment. The obtained chemical and isotopic data for methane in free gas of groundwater samples provide an excellent baseline against which potential future impact of deeper stray gases on shallow aquifers can be assessed.

An additional useful parameter for distinguishing gases from production zones, from the intermediate zone, and from shallow aquifers is the gas wetness defined as the concentration of ethane (C<sub>2</sub>) + propane (C<sub>3</sub>) + butane (C<sub>4</sub>) + pentane (C<sub>5</sub>) divided by the sum of concentrations of all n-alkanes including methane (C<sub>1</sub> to C<sub>5</sub>). A gas comprised mainly of methane with only traces of ethane would result in a gas wetness parameter close to 0, whereas more thermogenic gases with appreciable concentrations of ethane and higher n-alkanes would yield much higher wetness values. Free gases associated with shallow groundwater of this study and that by Cheung et al.<sup>7</sup> displayed generally a wetness value of 0.3 and average  $\delta^{13}\text{C}$  values of methane of -68 ‰ indicating a dry gas of biogenic origin. Gases from two coalbed methane plays in Alberta were found to have an average gas wetness between 6.0 (Horseshoe Canyon Formation) and 8.2 (Manville Formation) and average  $\delta^{13}\text{C}$  values of methane of -54 and -49 ‰, respectively<sup>7</sup>. Average wetness parameters for three shale gas containing formations in Western Canada varied widely from 0.2 (Horn River) to 8.8 (Montney), but the average  $\delta^{13}\text{C}$  values of methane were with -40 to -32 ‰<sup>8</sup> consistently much higher than those for methane from the intermediate and shallow groundwater zones.

#### 4. Conclusions

The isotopic composition of the obtained groundwater samples indicates that groundwater is of meteoric origin and that there was only limited impact of evaporation during recharge. Methane was found frequently in groundwater displaying highly variable concentrations. Isotopic analyses indicated that methane in shallow groundwater is predominantly of biogenic origin. In contrast, methane from the intermediate zone and from coalbed methane and shale gas production zones in Western Canada has distinct average wetness parameters and carbon isotope ratios. Hence we conclude that the combination of the wetness parameter and the  $\delta^{13}\text{C}$  value of methane can be an effective approach for tracing stray gas leakage, provided that baseline data have been obtained and that no additional isotope effects occur due to methane oxidation or gas diffusion.

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