Sources, trends, and fate of methane in shallow aquifers of Alberta, Canada

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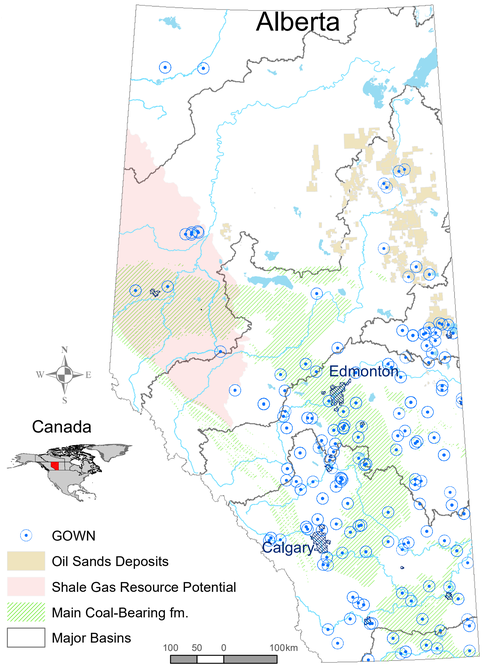
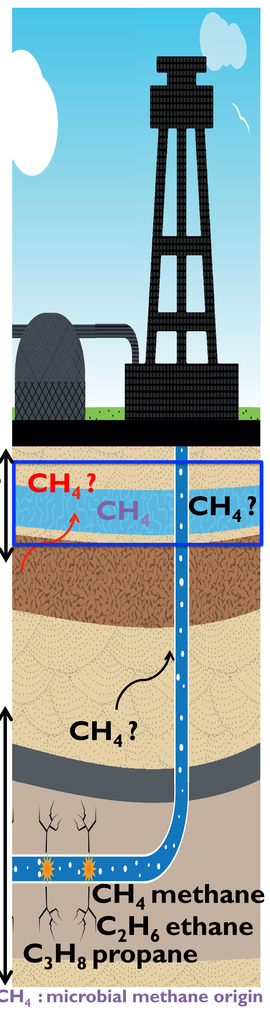
Due to concerns regarding potential impacts from the development of natural gas from unconventional hydrocarbon resources on groundwater systems in North America and elsewhere, it is crucial to improve methods for Environmental Baseline Assessment (EBA). Subsequent deviations from groundwater conditions defined from EBA could indicate migration of natural gas into the monitored groundwater systems. In collaboration with Alberta Environment and Parks, over 180 dedicated monitoring wells have been visited since 2006 resulting in an extensive high-quality database of aqueous and gaseous geochemical and isotopic compositions. Because methane is the main component of natural gas, it had been the principal target of our groundwater studies.

Our objectives were:

1) to assess the occurrence of methane in groundwater throughout the province of Alberta (Canada);
2) to use isotope techniques to track the predominant sources of methane;
3) to use a combination of chemical and multi-isotopic techniques and models to assess the fate of methane in groundwater;
4) to use probability for predicting the presence of methane in groundwater based on hydro-geochemical parameters in regions where no gas data exist.



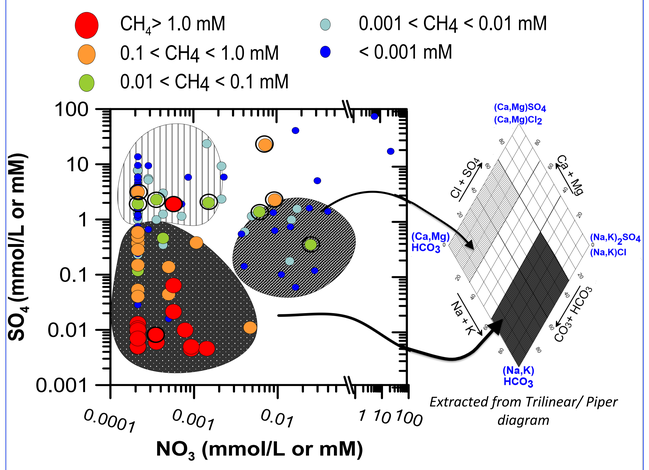


Groundwater systems & Environmental Baseline Assessment (EBA)

Occurrence of methane in groundwater [1]

Gas sampling procedure is found in Humez et al[1] and gaseous composition was determined by Gas Chromatography

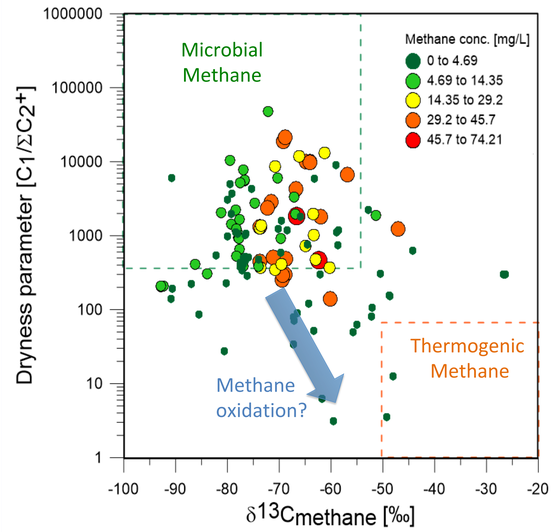
Methane is ubiquitous in the groundwater (gw) samples



Elevated methane occurs predominantly in:

- Na-HCO_3 or Na-HCO_3-Cl water types and;
- low/negligible terminal electron acceptors concentrations (e.g. NO_3^-, SO_4^{2-}) consistent with redox ladder concept.

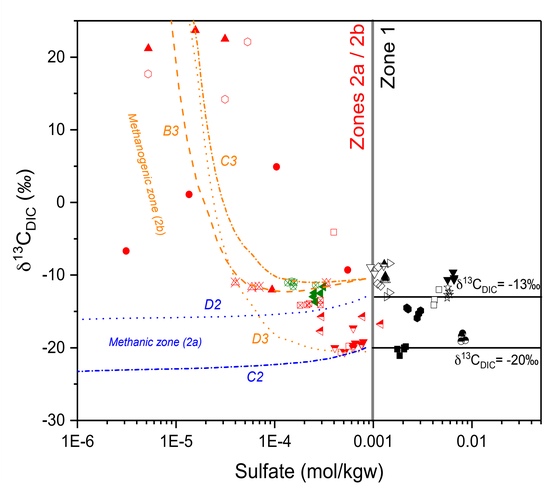
Source and fate of methane in groundwater [2,3]



Geochemical and isotopic model was developed using PHREEQC+ Basics code.
Two sources of methane were revealed:

Microbial methane from In-situ methanogenesis via CO_2 reduction;

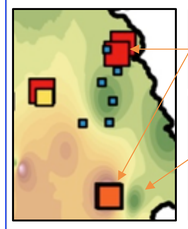
Migration of microbial methane followed by methane oxidation coupled with sulfate reduction processes
⇒"pseudo-thermogenic" methane isotopic signature



Legend:

Zone 1: post-oxic SO_4-rich groundwater
Zone 2a/2b: Reducing groundwater conditions/ elevated CH_4 conc. with advanced methanogenic conditions (2b)
C2,D2,B3,C3,D3 modeling scenarios[3]
Black symbols = gw samples in Zone 1;
Red symbols = gw samples in Zone 2a/2b;
Green symbols = outliers gw samples with low SO_4 and CH_4 contents.

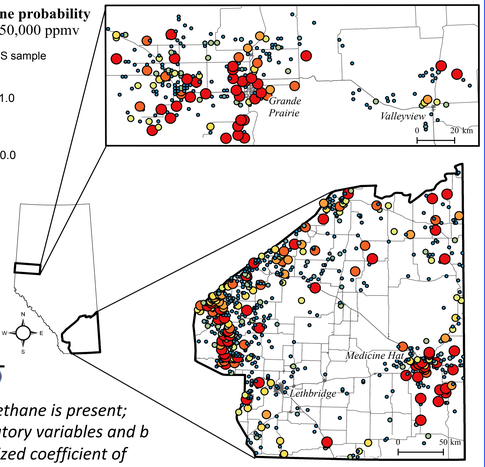
Methane prediction models [4]



Observed methane occurrence in dedicated monitoring networks

Predicted methane probability modelled from high-resolution groundwater quality data (public health network)

Can methane occurrence in groundwater be reliably forecasted to generate an environmental baseline?



$$P = \frac{e^{(b_0 + b_1X_1 + b_2X_2 + \ldots)}}{1 + e^{(b_0 + b_1X_1 + b_2X_2 + \ldots)}}$$

P is the probability that methane is present; X the vector of the explanatory variables and b the vector of the standardized coefficient of these explanatory variables

The Logistic Regression approach is able to extend EBA to sectors where relevant groundwater parameters such as CH_4 concentrations are not measured

Conclusion: Methane of microbial origin is ubiquitous in Alberta groundwater. Combining hydrochemistry, in particular redox-sensitive species and multi-isotope tools represent an excellent approach to accurately assess methane formation, trends and fates in groundwater of Alberta.

References: 1) Humez et al., *Hydrol. Earth Syst. Sci.* **2016**, *20*, 2759-2777; 2) Humez et al. , *Science of The Total Environment* **2016**, *541*, 1253-1268; 3) Humez et al., *Journal of Contaminant Hydrology* **2019**, *226*, 103525; 4) Humez et al., *Environmental Science & Technology* **2019,** *53,* 12914-12922.