

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

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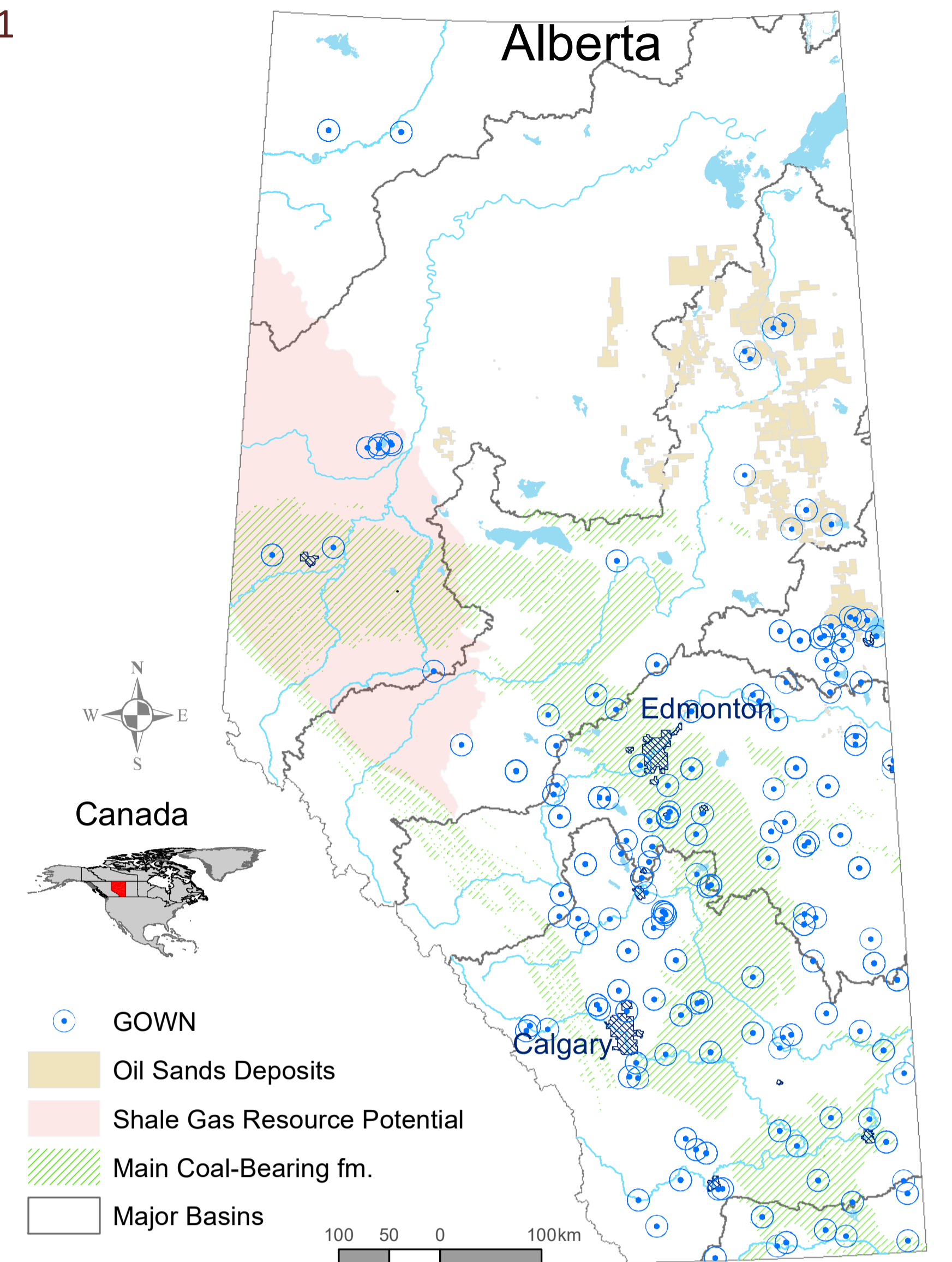
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Due to concerns regarding potential impacts from the development of natural gas from unconventional hydrocarbon resources on groundwater systems in North America and elsewhere, it is crucial to improve methods for Environmental Baseline Assessment (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.

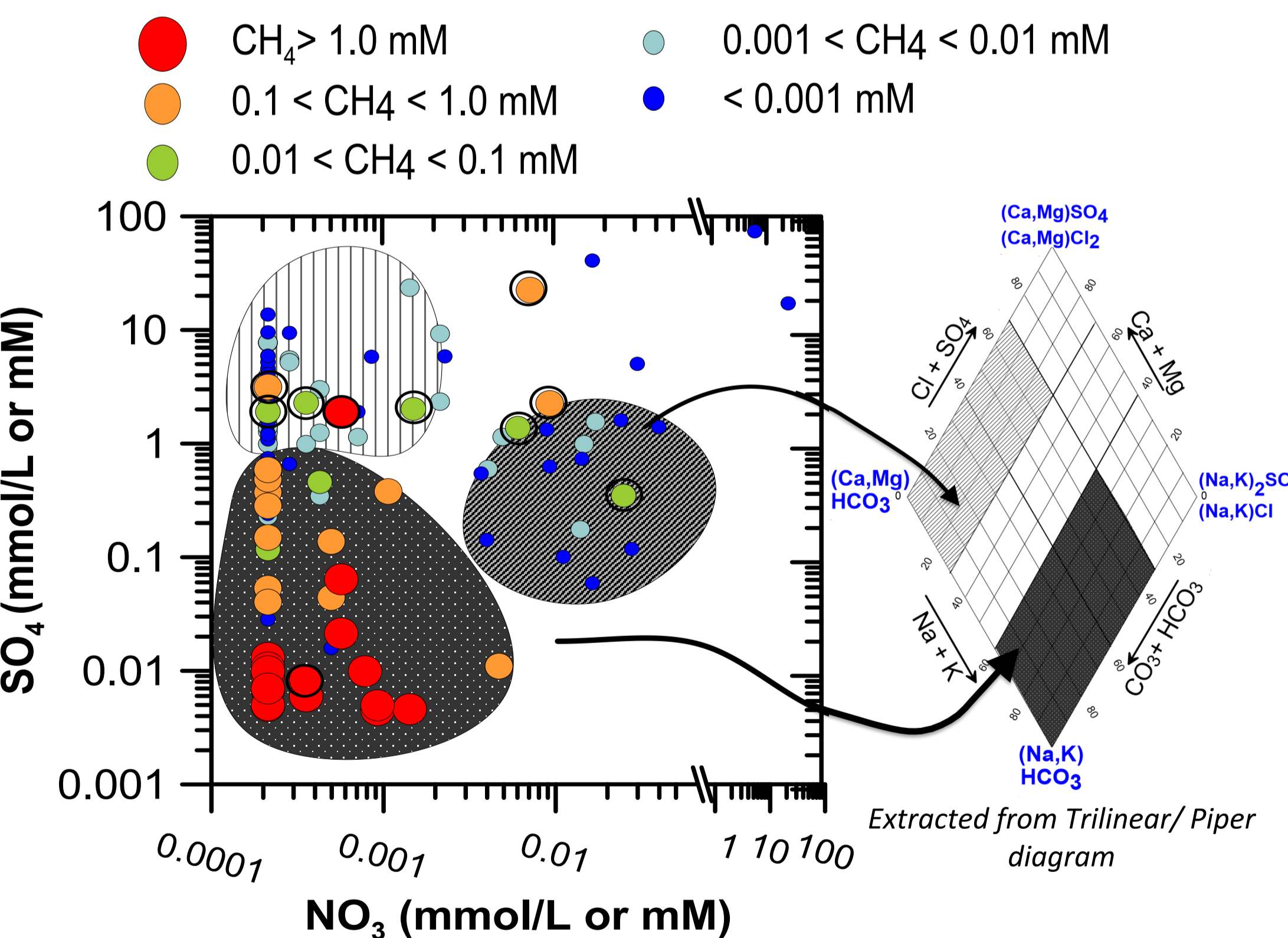


Groundwater systems & Environmental Baseline Assessment (EBA)

Occurrence of methane in groundwater¹

Gas sampling procedure is found in Humez et al¹ and gaseous composition was determined by Gas Chromatography

Methane is ubiquitous in the groundwater (gw) samples

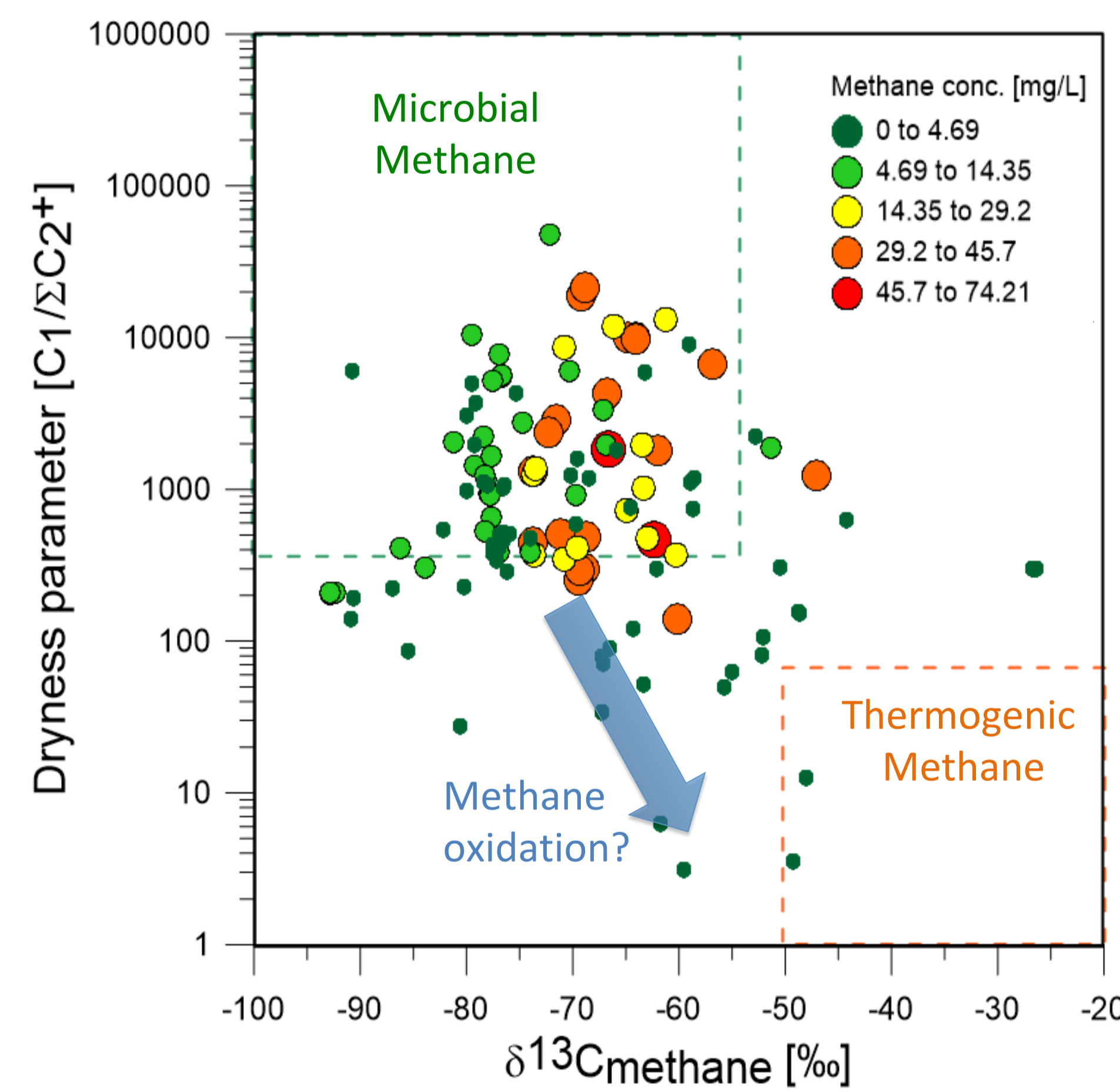


Elevated methane occurs predominantly in:

- Na-HCO₃ or Na-HCO₃-Cl water types and;
- low/negligible terminal electron acceptors concentrations (e.g. NO₃⁻, SO₄²⁻) consistent with redox ladder concept.

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.

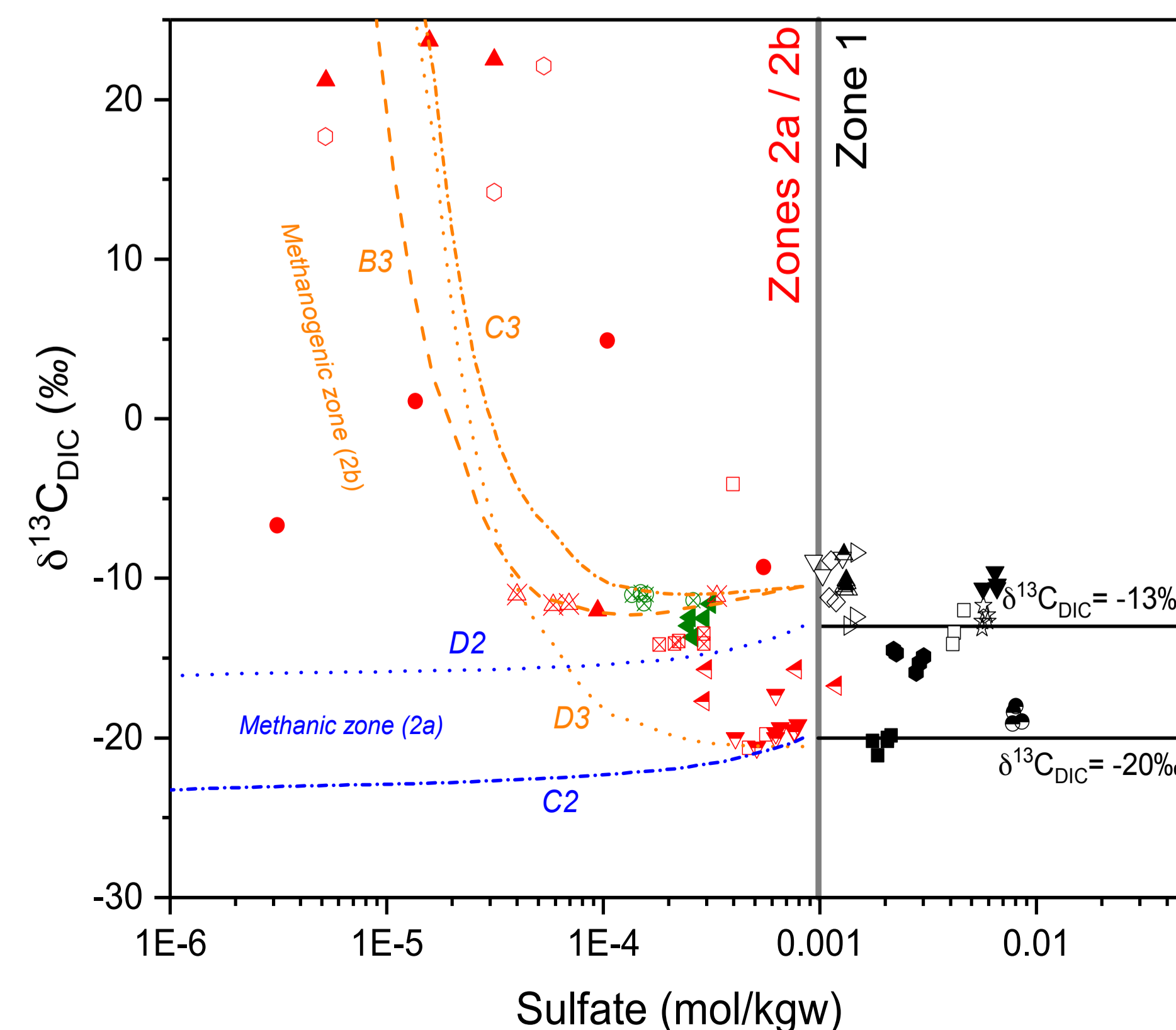
Source and fate of methane in groundwater^{2,3}



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

Microbial methane from In-situ methanogenesis via CO₂ reduction;

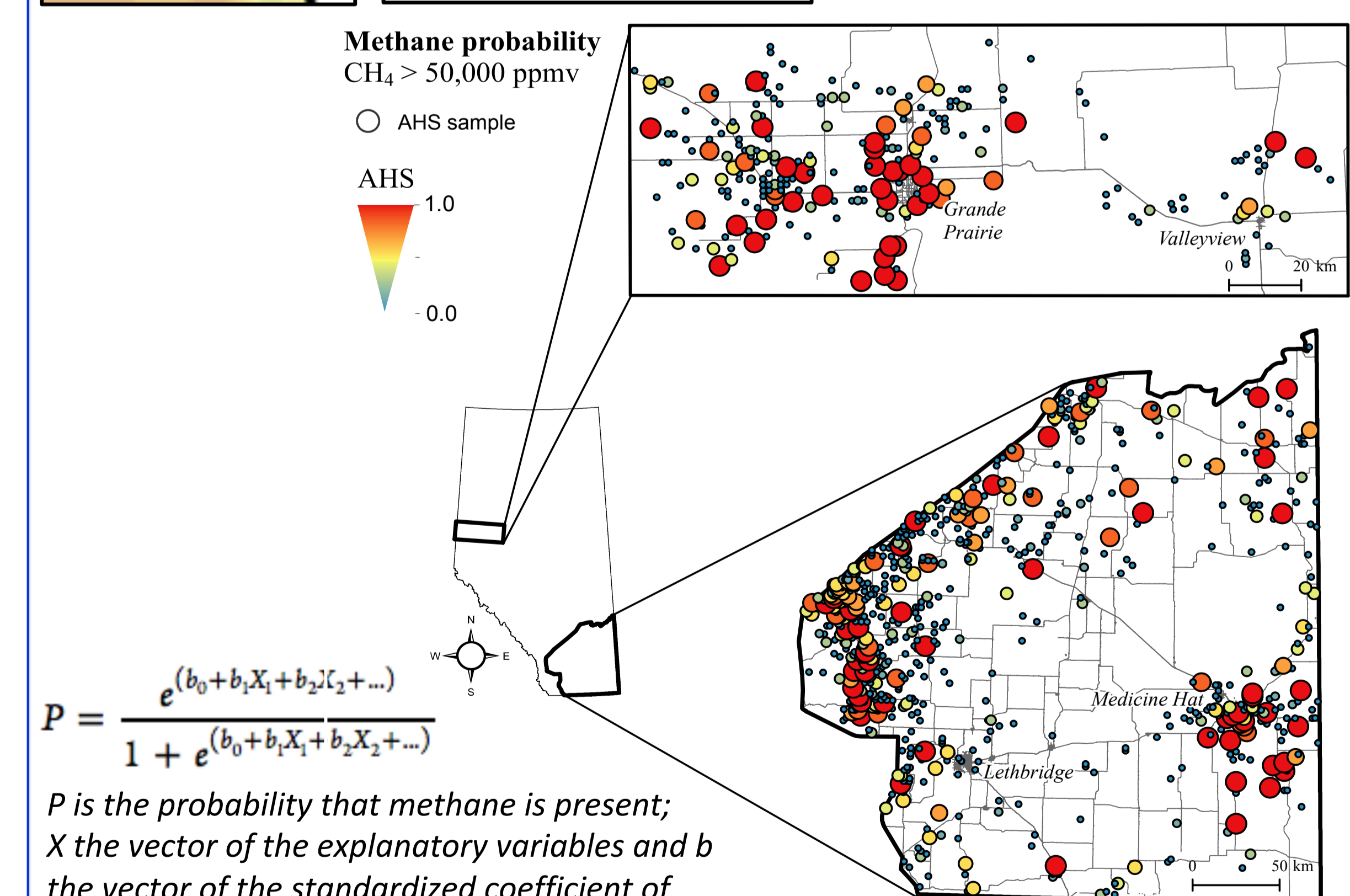
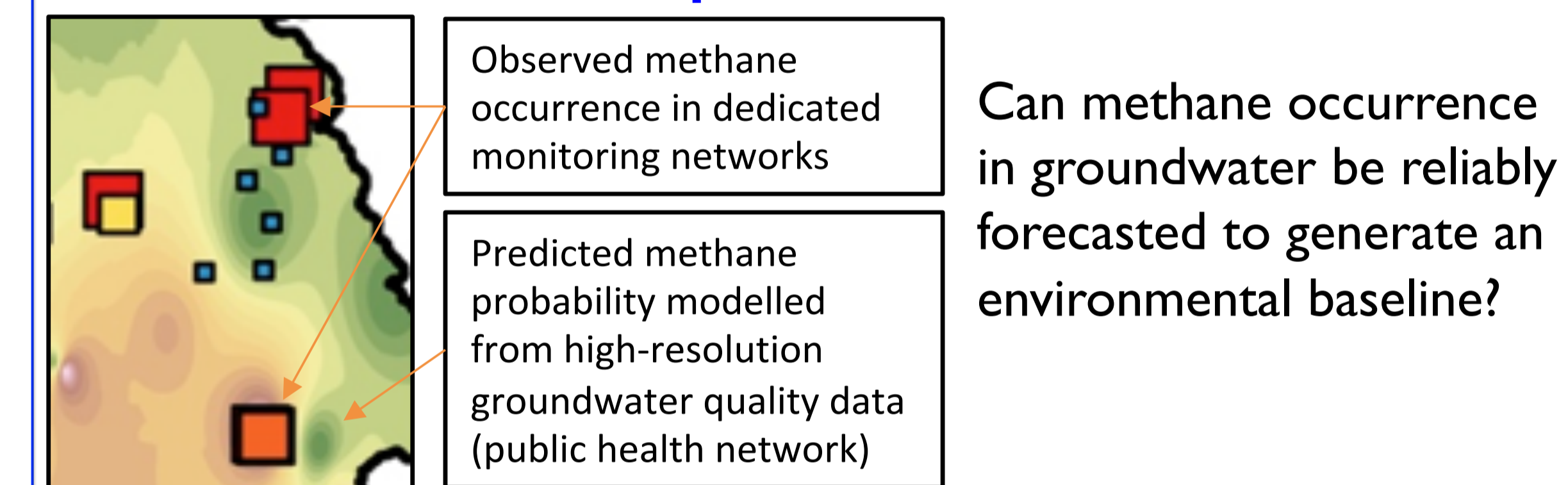
Migration of microbial methane followed by methane oxidation coupled with sulfate reduction processes ⇒ "pseudo-thermogenic" methane isotopic signature



Legend:

Zone 1: post-oxic SO₄-rich groundwater
Zone 2a/2b: Reducing groundwater conditions/ elevated CH₄ conc. with advanced methanogenic conditions (2b)
 C2, D2, B3, C3, D3 modeling scenarios³
 Black symbols = gw samples in Zone 1;
 Red symbols = gw samples in Zone 2a/2b;
 Green symbols = outliers gw samples with low SO₄ and CH₄ contents.

Methane prediction models⁴



$$P = \frac{e^{(b_0 + b_1 X_1 + b_2 X_2 + \dots)}}{1 + e^{(b_0 + b_1 X_1 + b_2 X_2 + \dots)}}$$

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 CH₄ 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.

