



## **The distribution of methane in groundwater in Alberta (Canada) and associated aqueous geochemistry conditions**

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Development of unconventional energy resources such as shale gas and coalbed methane has generated some public concern with regard to the protection of groundwater and surface water resources from leakage of stray gas from the deep subsurface. In terms of environmental impact to and risk assessment of shallow groundwater resources, the ultimate challenge is to distinguish: (a) natural in-situ production of biogenic methane, (b) biogenic or thermogenic methane migration into shallow aquifers due to natural causes, and (c) thermogenic methane migration from deep sources due to human activities associated with the exploitation of conventional or unconventional oil and gas resources. We have conducted a NSERC-ANR co-funded baseline study investigating the occurrence of methane in shallow groundwater of Alberta (Canada), a province with a long record of conventional and unconventional hydrocarbon exploration. Our objective was to assess the occurrence and sources of methane in shallow groundwaters and to also characterize the hydrochemical environment in which the methane was formed or transformed through redox processes. Ultimately our aim was to determine whether methane was formed in-situ or whether it migrated from deeper formations into shallow aquifers. Combining hydrochemical and dissolved and free geochemical gas data from 372 groundwater samples obtained from 186 monitoring wells of the provincial groundwater observation well network (GOWN) in Alberta, it was found that methane is ubiquitous in groundwater in Alberta and is predominantly of biogenic origin. The highest concentrations of dissolved biogenic methane ( $> 0.01$  mM or  $> 0.2$  mg/L), characterized by  $\delta^{13}\text{CCH}_4$  values  $< -55\text{‰}$  occurred in anoxic Na-Cl, Na- $\text{HCO}_3$  and Na- $\text{HCO}_3$ -Cl type groundwater with negligible concentrations of nitrate and sulfate suggesting that methane was formed in-situ under methanogenic conditions consistent with the redox ladder concept. Despite quite variable gas concentrations and a wide range of  $\delta^{13}\text{CCH}_4$  values in baseline groundwater samples, no conclusive evidence was found for deep thermogenic gas that had migrated in significant amounts into shallow aquifers either naturally or via anthropogenically induced pathways. This study shows that the combined interpretation of aqueous geochemistry data in concert with the chemical and isotopic composition of dissolved and/or free gas can yield unprecedented insights into formation or migration of methane in shallow groundwater. This enables the assessment of cross-formational methane migration and provides an understanding of alkane gas sources and pathways necessary for a stringent baseline definition in the context of current and future unconventional hydrocarbon exploration and exploitation.