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Identifying the source of methane and higher alkanes in groundwater of the St. Lawrence Platform, Saint-Édouard area, eastern Canada: a multi-isotope approach

Geneviève Bordeleau[1]. Christine Rivard[1], Denis Lavoie[1], René Lefebvre[2], Jason Ahad[1], Xiaomei Xu[3]

[1]Geological Survey of Canada, Natural Resources Canada, Quebec City, QC, Canada

[2]Institut National de la Recherche Scientifique (INRS), Quebec City, QC, Canada

[3]University of California, Irvine, CA, USA

Abstract

A multidisciplinary project was carried out to evaluate potential impacts to shallow groundwater quality from eventual shale gas exploration and exploitation in the Saint-Édouard area located in the St. Lawrence Lowlands near Quebec City, eastern Canada. Groundwater samples from residential wells and dedicated observation wells, as well as gas extracted from bedrock samples (from the drilling of observation wells) were collected. In addition to concentrations of various traditional compounds, a suite of isotopes was analyzed as part of a multi-isotope approach, aiming at identifying the origin of dissolved methane and higher alkanes in shallow aquifers. For groundwater, the suite of analyzed isotopes includes stable isotopes of water ($\delta^{18}O$, $\delta^{2}H$), of methane, ethane and propane ($\delta^{13}C$, $\delta^{2}H$), and of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC; $\delta^{13}C$), as well as radiocarbon (^{14}C) in methane and DIC. Analyses for gas extracted from bedrock samples include stable isotopes ($\delta^{13}C$, $\delta^{2}H$) of methane, ethane and propane, as well as ^{14}C in methane. Results were compared with local and regional data available for gas in deep formations, from the Utica Shale and overlying Lorraine Group shales.

Traditional tracers commonly used in similar studies (gas dryness ratio, methane stable isotopes) provided useful information on methane origin, but were not sufficient to resolve ambiguous origin in many wells. Using multiple lines of evidence (mainly $\delta^{13}C$-CH_4, $\delta^{2}H$-CH_4, $\delta^{13}C$-DIC, ^{14}C-DIC and ^{14}C-CH_4) in groundwater and shallow bedrock gas samples helped unravel the origin of methane in groundwater (thermogenic versus microbial), the source of methane (local bedrock aquifer versus migration from greater depth), and the processes affecting its isotopic signature. Results show that most of the methane in shallow groundwater is of microbial origin, and that this microbial methane was mainly produced in the distant geological past. Various processes affecting the isotopic signature of methane, namely late-stage methanogenesis and, to a much lesser extent, methane oxidation, are responsible for ambiguous methane isotopic signatures. A contribution of thermogenic gas occurs in 15% of the wells, but both the thermogenic and the microbial methane originate from the local aquifer rather than migration from greater depths, with the exception of one sample which had an isotopic ratio corresponding to greater depths. To the best of our knowledge, this is the first report of such a diverse set of parameters analyzed both in groundwater and shallow bedrock.