

Source of dissolved hydrocarbons in groundwater— isotopic fingerprinting

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Shale gas exploration in southern Quebec (eastern Canada) focussed on the Upper Ordovician Utica Shale. Shallow groundwater has regionally variable and locally high levels of naturally occurring dissolved methane, with sometimes thermogenic C2 and C3. In our study area, the bedrock consists of Upper Ordovician clastics and the Utica Shale is present at depth of 2 km. The organic matter in the shallow bedrock is marine Type II kerogen. Hydrocarbon extracts from shallow cores (3-150 m) have shown an upward decrease in total volatiles (C1+C2+C3) together with an increase in the gas dryness ratio (C1/C2+C3). The $\delta^{13}\text{C}_{\text{VPDB}}$ values of C1 change from thermogenic values ($\approx -50\text{‰}$) for deeper samples, to more microbial values ($< -60\text{‰}$) at shallow depths with a similar $\delta^2\text{H}_{\text{VSMOW}}$ trend of more negative values at shallower depths. The $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^2\text{H}_{\text{VSMOW}}$ values of C1 indicate that core samples at shallow depths recorded a microbial influence. It is proposed that diffusion and some microbial degradation of hydrocarbons are responsible for 1) the decrease of rock volatiles and 2) the *in situ* generation of microbial methane in the shales at shallow depths that mixed with the *in situ* thermogenic methane. Thermogenic and biogenic volatiles found in groundwater can thus originate from shallow bedrock pores and fractures with short migration pathways.