

Gorody, A. W. , 2013, Stable isotope tracers useful for addressing groundwater impacts of oil and gas operations (Invited), Houston Geological Society, Nov. 23, 2013

Abstract:

Combined measurements of both dissolved element concentrations and stable isotope ratios are essential tools used to address potential groundwater impacts. When applied systematically, such measurements help to identify sources of impacted groundwater, to recognize source fluid mixtures, and to differentiate the effects of dilution from natural attenuation in response to remediation activities. Samples collected and analyzed for this purpose should represent end-member compositions of all potential fluid sources and any associated free and/or dissolved gases. These include water from domestic water wells, monitor wells, mud logging samples collected while drilling, produced fluids, and any casing head gases occurring at elevated pressures.

An example of a systematic approach for addressing sources of free and dissolved methane in groundwater includes using the following stable isotope analytical set: $\delta^{13}\text{C}_{\text{methane}}$, $\delta^2\text{H}_{\text{methane}}$, $\delta^2\text{H}_{\text{water}}$, $\delta^{18}\text{O}_{\text{water}}$, and $\delta^{13}\text{C}_{\text{DIC}}$.

- Stable isotope ratios of oxygen and hydrogen in water are used in conjunction with major ion and trace metal analysis to address hydrologic settings (e.g. source fluids derived from either shallow vs. deeper aquifers or recharge vs. discharge zones).
- The stable isotope ratios of hydrogen in both water and dissolved methane is used to differentiate biogenic (via fermentation or CO₂ reduction) vs. thermogenic sources, to identify end member stray gas source compositions, and to recognize enrichment fractionation of residual hydrocarbons associated with bacterially-mediated oxidation (natural attenuation).
- Stable isotope ratios of carbon and hydrogen in methane are used to identify contaminant sources, mixed methane sources, and to further verify enrichment fractionation of residual hydrocarbons associated with bacterially-mediated oxidation.
- The stable isotope ratio of carbon in dissolved inorganic carbon (DIC) is used to address contaminant gas sources containing measurable CO₂ and to recognize depletion fractionation associated with bacterially-mediated oxidation.
- In addition to stable isotope analyses, results derived from chromatographic analysis of fixed gases and hydrocarbons are also vital. For example, the presence of methane homologs larger than ethane, and gas composition parameters such as wetness, ethane/methane ratios, ethane/propane ratios, and butane and pentane isomer ratios are used together to identify the presence of stray thermogenic gas in samples and to recognize the effects of natural attenuation.

Because the groundwater environment intercepted by water wells interacts dynamically to affect stray gas sample composition as described, repeated sampling and analysis of both gas and groundwater sources is a necessary component of all contaminant source gas investigations. Periodic sampling will satisfactorily reveal temporal trends that help differentiate the effects of mixing, dilution, and natural attenuation.

In addition to the stable isotope ratios of oxygen and hydrogen in groundwater water, other stable isotope analyses are being developed to help address potential contaminant sources in groundwater. Most recently, 87/86Sr and 11/10B analyses have been used to differentiate fluids derived from various Devonian aquifers in the Appalachian basin. Such analyses could be particularly useful when used in conjunction with measurements of dissolved Sr, B, Cl, and Br concentrations in groundwater to identify stray aqueous fluid sources in water wells.