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## The Use of Stable Isotope Tracers to Address Groundwater Impacts of Oil and Gas Operations

Combined measurements of both dissolved element concentrations and stable isotope ratios are essential tools used to address potential groundwater impacts of oil and gas operations. 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 shallow versus deeper aquifers or recharge versus discharge zones).
- The stable isotope ratios of hydrogen in both water and dissolved methane are used to differentiate biogenic (via fermentation or CO<sub>2</sub> reduction) versus 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 and 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 CO<sub>2</sub> 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.

*In addition to the stable isotope ratios of oxygen and hydrogen in groundwater, other stable isotope analyses are being developed to help address potential contaminant sources.*

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 are necessary components 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, other stable isotope analyses are being developed to help address potential contaminant sources. Most recently, <sup>87/86</sup>Sr and <sup>11/10</sup>B 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. ■

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**Biographical Sketch**

Anthony W. Gorody is a forensic geoscientist with 30 years of diverse international and domestic industry experience dedicated to evaluating groundwater and natural gas resources. An industry leader in baseline environmental measurement and monitoring programs, Dr. Gorody provides training and consulting services



for assessing technical and environmental risks related to the acquisition, drilling, and development of both unconventional and conventional natural gas properties. In that capacity, he is a technical advisor and consultant to oil and gas producers, state and federal regulators, and community development groups. He maintains working relationships with many of the largest environmental service companies in the Rocky and Appalachian mountain areas.

Dr. Gorody’s forensic expertise relates to state-of-the-art geochemical fingerprinting, sampling, and analytical techniques needed to address sources of groundwater contamination and the effectiveness of remediation methods. In association with Ellington and Associates Inc., he provides the only on-site third party mud-logger auditing services available in the United States.

Dr. Gorody is licensed as a professional geologist in Texas, Pennsylvania, and Wyoming. His experience is based on projects conducted in the Washakie, Wind River, Powder River, Green River, San Juan, Raton, Piceance, Denver-Julesberg, Fort Worth, Rio Grande, Black Warrior, and Appalachian basins, and the Gulf Coast Tertiary, deep Gulf of Mexico, and the San Rafael Swell. His experience in international projects includes the Persian Gulf, North Sea, Baltic, Telkwa (BC), Comox (BC), and Hat Creek (BC) Basins.