



NEW YORK STATE WATER RESOURCES INSTITUTE

Department of Earth and Atmospheric Sciences

1123 Bradfield Hall, Cornell University
Ithaca, NY 14853-1901
<http://wri.eas.cornell.edu>

Tel: (607) 255-3034
Fax: (607) 255-2016
Email: nyswri@cornell.edu

The Role of Isotopes in Monitoring Water Quality Impacts Associated with Shale Gas Drilling

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Methane is one of the most common contaminants of groundwater and private drinking water wells. Methane contamination is usually due to natural causes; however, it can also be the result of drilling activities, including shale gas drilling. Monitoring techniques exist for detecting methane and, in some cases, identifying potential sources of methane contamination. These techniques involve measurement of stable isotopes of carbon (C) and hydrogen (H) within methane (CH₄) and related compounds, such as carbon dioxide (CO₂), water (H₂O), ethane (C₂H₆) and other hydrocarbons. The goal of this type of monitoring is to aid water well owners who wish to distinguish methane contamination that arises naturally from contamination resulting from nearby drilling activities.

While stable isotope monitoring can provide valuable information in the event of water contamination, it also has significant limitations. Conclusive results generally require extensive and coordinated sampling, incorporation of additional data related to geology, hydrology, and chemistry, and expertise in data interpretation. Below, we discuss these techniques in more detail within the context of shale gas drilling activities in New York, as well as their uses and limitations.

Background and Theory (briefly)

New York State has a long history of natural gas drilling and exploration. Some modern shale gas drilling practices, such as high volume hydraulic fracturing, are relatively new and present unique challenges. Other practices, such as near-surface vertical drilling,

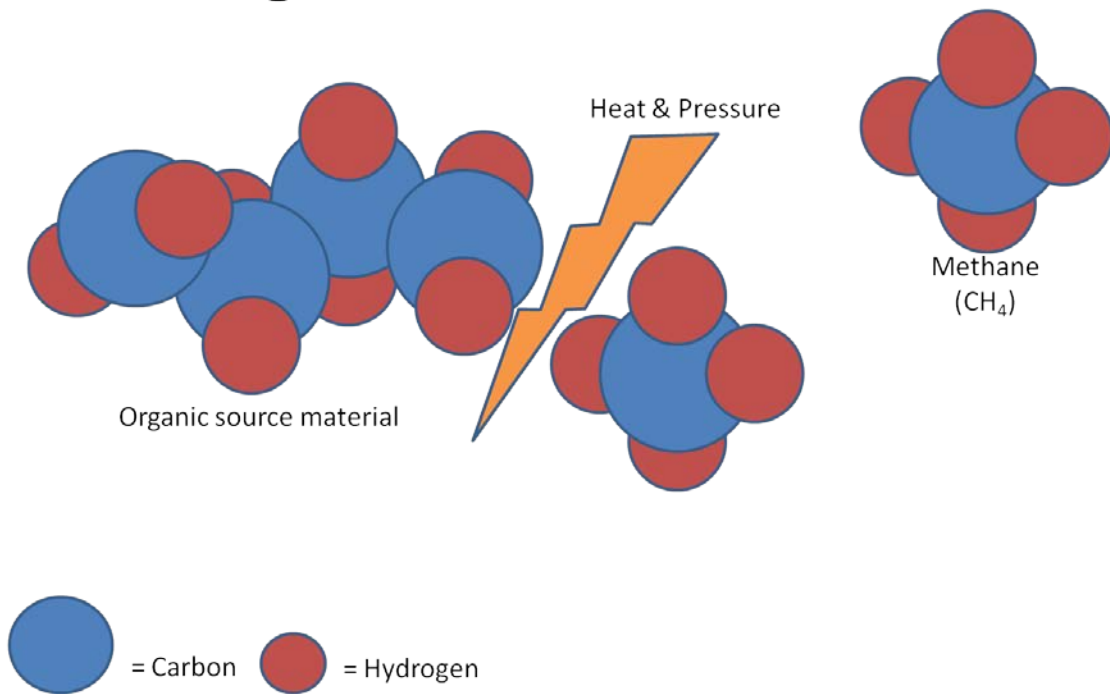
present challenges and have potential negative consequences that have been recognized in the past. Methane contamination of private water wells, possibly as a result of conventional, vertical drilling, has been previously documented in western NY and northwestern PA (Harrison 1983; Harrison 1985; Hewitt 1986). Elsewhere, it has been shown that gas drilling and storage operations have the potential to result in methane contamination of nearby ground and well waters (Taylor 2000; Breen 2007; Sharma 2008; Thyne 2008). In a majority of these cases, methane contamination is thought to arise from leakage from the well annulus and/or disruption and migration of methane reservoirs in near- surface or overlying formations. There are, no doubt, other documented instances of methane contamination in various gas fields, but the above references suffice to illustrate the issue.

In many places, groundwater naturally contains significant concentrations of methane. High concentrations of methane, sometimes at explosive levels, are known to occur in both NY and PA, and elsewhere (Osborn 2010; WV USGS 2006). This makes the mere detection of methane in private water wells an inadequate test for determining whether gas drilling has caused water contamination. Since methane contamination can originate from both natural and industrial processes, a more sensitive method is needed for determining the gas source.

Techniques which explore and analyze stable isotope signatures of methane and related molecules can be used to help determine the source of methane contamination. These techniques work because, isotopically, not all methane is the same. In subtle ways, methane molecules can differ depending on how and where they are formed, and the processes they are subjected to.

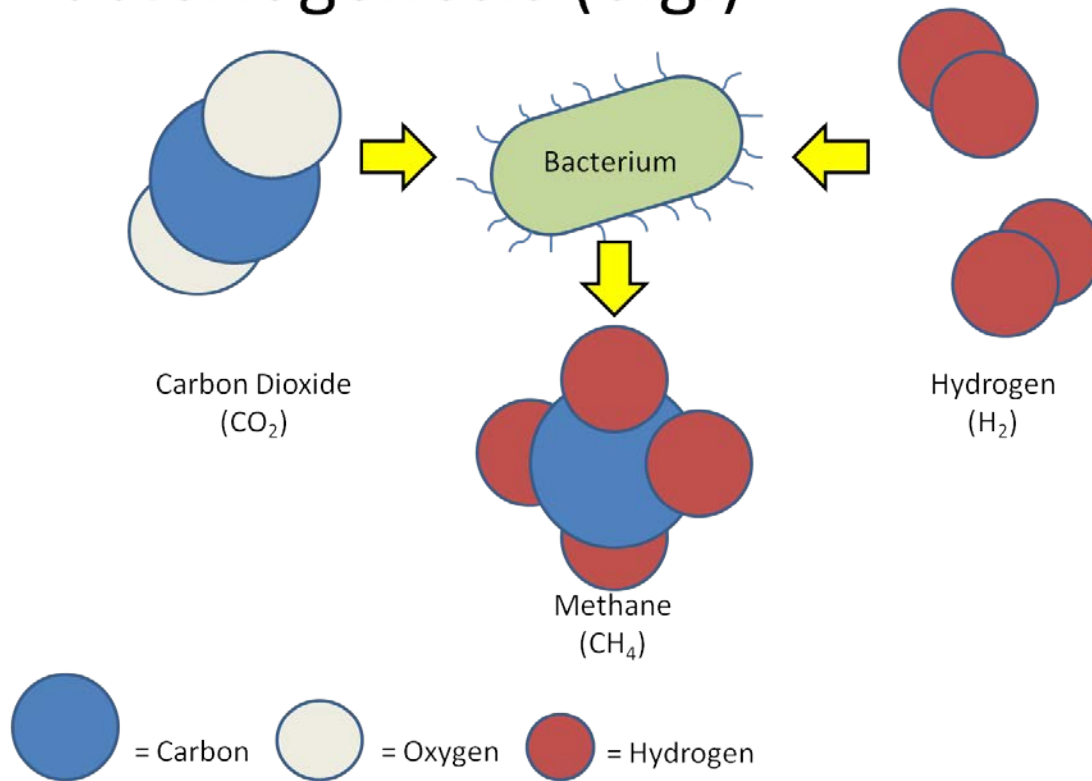
Fundamentally, methane is created one of two ways. Thermogenic methane forms when organic matter present in a sedimentary geological formation is subjected to heat and pressure. The stress of this geological “maturation” process causes the methane molecule (CH_4) to break off of larger organic compounds.

Thermogenesis



Bacteriogenic methane, on the other hand, forms as a result of microbial metabolic processes in which compounds such as carbon dioxide (CO₂), hydrogen (H₂), and acetate are converted into CH₄ and water (H₂O) in order to produce energy.

Bacteriogenesis (e.g.)

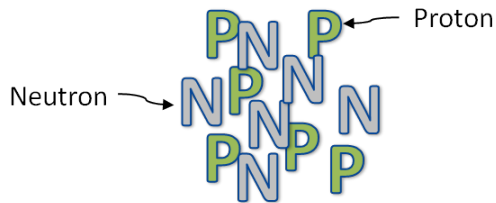


These two main types of methane, thermogenic and bacteriogenic, contain characteristic concentrations of stable isotopes – carbon and hydrogen molecules with an unusual number of neutrons.

Stable isotopes can generally be divided into two categories. “Light” isotopes are elements that have nuclei containing the normal number of protons and neutrons. In the case of carbon, each nucleus contains 6 protons and 6 neutrons. “Heavy” isotopes, however, contain an extra neutron relative to their “lighter” counterparts. A heavy nucleus of carbon, for example, contains 6 protons and 7 neutrons, imparting additional mass to the molecule. Heavy isotopes move more slowly, and form bonds that are more difficult to break relative to light isotopes.

Isotopes

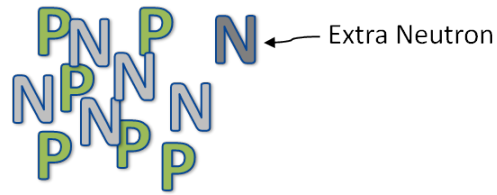
Light



Carbon (^{12}C) Nucleus
6 Protons
6 Neutrons

$$\text{Mass} = 6 + 6 = 12$$

Heavy



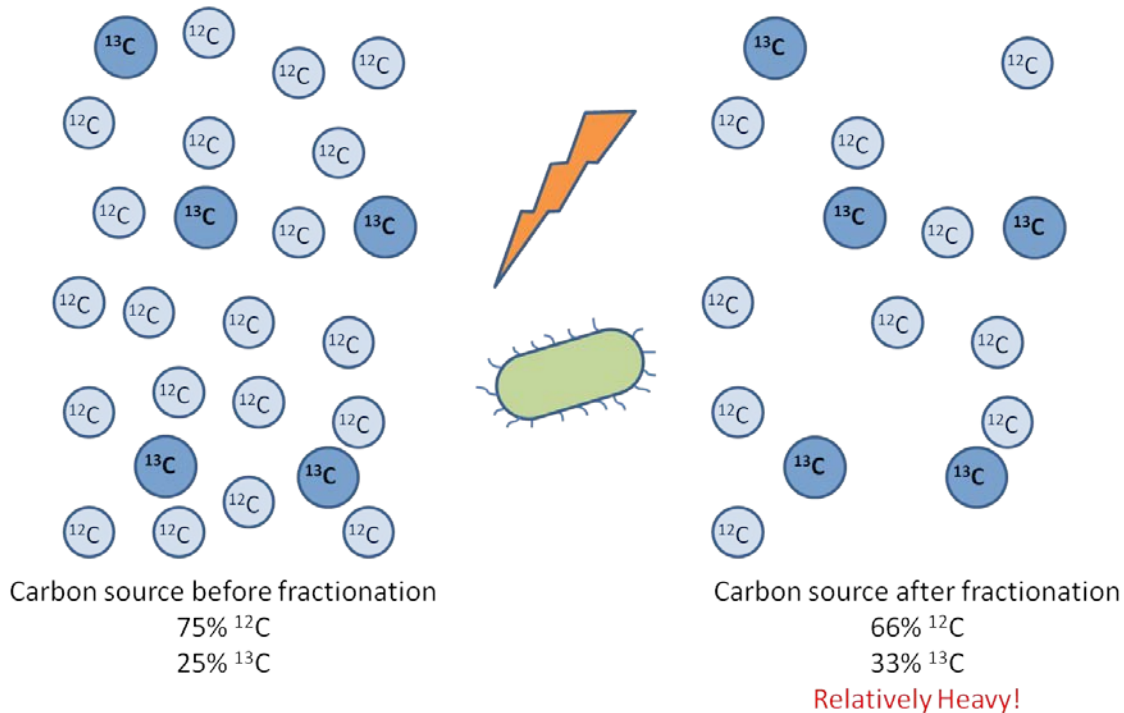
Carbon (^{13}C) Nucleus
6 Protons
7 Neutrons

$$\text{Mass} = 6 + 7 = 13$$

This is important because it leads to “fractionation”. Fractionation refers to the process by which lighter isotopes are preferentially selected during transformation processes, such as during the breakdown of complex organic material into simpler compounds, and during the use of various compounds by bacteria. In other words, heavy isotopes get left behind during the process of methane formation. Methane molecules formed both thermogenically and bacteriogenically contain more light H and C relative to the source material from which the methane was made (such as acetate, or organic material within shale).

The amount of fractionation that has occurred is denoted with the symbol “ δ ”.

Fractionation



The theory and science behind the detection of methane, and the use of isotopes as a means of determining gas origin, goes back many decades, and a complete review is beyond our scope here. For more complete discussions of this work, see Whiticar (1999). Osborn and McIntosh (2010) also review the forensic utility of isotopes, and frame the discussion within the context of northeastern shales. Breen et. al. (2007) is an excellent example of the use of these techniques for diagnosing gas contamination in private water wells and serves to illustrate both their potential and limitations. Additional sources of information on isotopes in general are provided below.

Making a Distinction: Thermogenic v Bacteriogenic Methane Origins

As described above, thermogenic methane is generated by heat and pressure applied to organic material over hundreds of millions of years. Complex organic material is

slowly broken down into successively simpler molecules, including pentane, butane, propane, and ethane. These hydrocarbon compounds will be referred to as C₂₊ compounds, since they all contain at least two carbon atoms. Methane, which contains only one carbon atom, is the final and simplest hydrocarbon that forms as a result of this process. Thermogenic gas generally contains a mixture of these compounds (CH₄ and C₂₊). Bacteriogenic methane, on the other hand, results from the metabolic transformation of CO₂ and/or organic acids such as acetate. Generally, bacterial transformations do not result in the formation of C₂₊ hydrocarbons. Therefore, the presence or absence of C₂₊ hydrocarbons can be used as a rough indicator of gas origin. Water well methane contamination with measureable C₂₊ concentrations could indicate the presence of thermogenic gas. The absence of C₂₊ compounds may support a bacteriogenic origin for contaminating gas. By itself, however, C₂₊ concentration is rarely enough to conclude gas origin with certainty.

Besides the C₂₊ content of the gas in general, carbon isotope fractionation ($\delta^{13}\text{C}$) within the CH₄ molecule is often the most informative parameter when trying to distinguish thermogenic from bacteriogenic gas origin. For CH₄ of thermogenic origin, the fractionation of C is related to the C content of the source material (e.g. shale and C₂₊ compounds). Therefore, the $\delta^{13}\text{C}$ of methane contamination can be compared to the $\delta^{13}\text{C}$ of suspected source materials, such as shale formations or gas reservoirs known to exist within the area of the well. The $\delta^{13}\text{C}$ of bacteriogenic methane, on the other hand, is related to the C content of bacterial metabolic substrates such as CO₂ and acetate. Bacteria often create even more pronounced fractionation of C isotopes relative to thermogenic processes. This is because bacteria strongly prefer lighter C isotopes, and also because source metabolic substrates (CO₂ and acetate) are often themselves products of bacterial respiration, which in turn are subject to fractionation. Thus, contaminant CH₄ that has highly fractionated C indicates a bacterial origin. Comparing $\delta^{13}\text{C}$ values of contaminant CH₄ with source materials, such as geologic organic material, C₂₊ compounds, and CO₂ and acetate from possible formation reservoirs, may also help to determine methane origin.

Isotope fractionation values of hydrogen are also used to further characterize methane origins. "Heavy" hydrogen is called deuterium, and the symbol δD is used to indicate the value of its fractionation. Like $\delta^{13}\text{C}$, the δD of thermogenic methane is related to

the δD of the source material (e.g. shale and C_{2+} compounds). However, δD values of source materials can range widely even within geographically closely related samples. The δD of bacteriogenic methane, like before, is related to the H content of bacterial metabolic substrates such as H_2O , H_2 and acetate. Of particular interest are the isotopic properties of H_2O . Freshwater has a very different δD value compared to marine water. This is because freshwater comes predominantly from precipitation, and because precipitation results in strong fractionation of hydrogen. Bacteriogenic CH_4 with hydrogen derived from freshwater (acetoclastic methanogenesis) can sometimes be identified on the basis of this strong δD fractionation. Bacteriogenic CH_4 with hydrogen derived from marine water (hydrogenotrophic methanogenesis), on the other hand, does not produce such distinct δD values. Therefore, δD values of contaminant CH_4 may indicate a high degree of fractionation indicative of some types of bacteriogenic methane formation. Other values for δD , however, are not helpful in distinguishing between thermogenic and certain bacteriogenic methane formation processes.

Confounding Variables: Mixing, Migration, and Oxidation

In an ideal world, the techniques described above would provide sufficient evidence to unambiguously differentiate between thermogenic and bacteriogenic methane. They often do. However, confounding circumstances sometimes occur that make methane characterization more difficult, and less certain. The processes of mixing, migration and bacterial oxidation all have the potential to impede a clear diagnosis of methane contamination.

Mixing refers to a situation in which gases from different sources combine within one geologic or groundwater reservoir or water well. Mixtures of gases could be combinations of thermogenic and bacteriogenic gas, or combinations of either kind of gas from more than one source. The isotopic composition of mixed gas no longer resembles the often distinct signature of a single source.

Migration refers to the movement of gas from one location to another over varying distances and timescales. As with thermogenic maturation and bacteriogenic

metabolic processes, migration can result in fractionation of carbon containing compounds. In the case of $\delta^{13}\text{C}$ values associated with CH_4 , for example, migration can enhance the fractionation of thermogenic gas as it moves from gas reservoirs to water wells, causing it to take on isotopic characteristics that are usually associated with bacteriogenic gas.

During oxidation, bacterial metabolic processes convert methane into CO_2 in order to produce energy. Just as bacteriogenic methane formation produces a highly fractionated methane pool relative to source material, bacterial oxidation of methane results in a less fractionated methane pool. “Light” methane is used and converted to CO_2 , while “heavy” methane is left behind. If bacteria capable of methane oxidation are present, they can significantly complicate the interpretation of $\delta^{13}\text{C}$ values.

Each of these processes, mixing, migration and oxidation can alter the isotopic composition of the methane gas, making unambiguous distinction between thermogenic and bacteriogenic methane difficult. These factors, in concert with natural uncertainty and variability in isotope characteristics as highlighted above, can combine to make the use of stable isotope techniques a challenge. To confidently diagnose methane contamination in private water wells, it is oftentimes useful to incorporate multiple isotope analyses with broader studies of geologic, hydrologic, and biogeochemical data.

Diagnosing Methane Contamination: Overall Strategy & Usefulness

Diagnosing methane contamination in groundwater and private drinking water wells is possible with the help of isotopic analyses. However, it is not necessarily an easy task, and can be limited by significant uncertainty.

In general, examination of gaseous C_2+ content coupled with CH_4 -associated $\delta^{13}\text{C}$ is not sufficient for accurate determination of gas origin in all cases. As several comprehensive studies indicate, it is often useful to combine these measurements with isotopic analyses of CH_4 -associated δD , as well as additional isotopic analyses of source

and formation materials such as ethane, H₂O, and CO₂ (Whiticar 1986; Whiticar 1999). Diagnosing methane subject to mixing, migration and/or oxidation presents a particular challenge. When these processes are suspected to be involved, additional geological, hydrological, and geochemical information has been used to support isotope data (Breen 2007).

As a tool to protect groundwater and owners of private water wells, these techniques appear best suited for use over larger areas in which multiple samples may be analyzed and compared. Confident diagnosis may in some cases require significant scientific expertise and expense. These techniques are less effective for diagnosing contamination of isolated water wells unless there is existing contextual data available. Earnest forensic analyses are likely to be employed only after contamination is thought to have occurred, and in cases where a significant number of complaints are filed, or where significant environmental or public health damage is suspected. As with most monitoring tools, stable isotopes are not useful for preventing contamination.

Annotated References

This list is in no way exhaustive. Rather, it attempts to provide a set of primary references that offer key pieces of information in building a clear understanding of the issue.

** Osborn, S.G. & McIntosh, J.C. Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin. *Appl. Geochem.* **2010**, *25*, 456-471.

- Gives evidence from both gas and liquid phase analysis for the thermogenic origin of methane in Devonian shales of Appalachia

Sharma, S. & Frost, C.D. Tracing coalbed natural gas-coproduced water using stable isotopes of carbon. *Ground Water.* **2008**, *46*, 329-334.

- Uses the fractionation of carbon in dissolved inorganic carbon as a diagnostic test for the migration of formation waters into rivers; depends on significant bacteriogenesis

Thyne, G. Review of Phase II Hydrogeologic Study. SBS LLC. **2008**.

<http://www.garfield-county.com/Index.aspx?page=1143>

- A report for Garfield County, CO that provides evidence for the cumulative impact of increasing gas well activity, specifically showing increased methane and chloride in water wells

** Breen, K.J.; Revesz, K.; Baldassare, F.J.; McAuley, S.D. Natural gases in ground water near Tioga Junction, Tioga County, North-Central Pennsylvania – Occurrence and Use of Isotopes to Determine Origins, 2005. *USGS Scientific Investigations Report 2207-5085*. **2007**.

<http://pubs.usgs.gov/sir/2007/5085/>

- A monitoring study in response to complaints of methane in private water wells in PA; shows the uses of stable isotopes, biogeochemistry and hydrogeology in determining potential contamination sources; also demonstrates limitations and difficulties associated with monitoring

Methane in West Virginia ground water. USGS Fact Sheet 2006-3011. **2006**.

<http://pubs.usgs.gov/fs/2006/3011/>

- Shows extent and severity of historic methane contamination of wells in WV, with links to coal mining activities

Taylor, S.W.; Sherwood Lollar, B.; Wassenaar, L.I. Bacteriogenic ethane in near-surface aquifers: implications for leaking hydrocarbon well bores. *Environ Sci & Technol*. **2000**. *34*, 4727-4732.

- Bacteriogenic vs thermogenic CH₄: utilizes a graph of $\delta^{13}\text{C}$ of ethane, rather than CH₄, plotted against the C₁/C₂₊ ratio. This is a variation on a theme that seems to have worked well for the samples in their study. They specifically address the presence of gas contamination in near surface aquifers as a possible result of well drilling. They conclude that contaminating gases are sometime present, but that they tend to originate from bacteriogenic sources located in overlying formations.

Whiticar, M.J. Carbon and hydrogen isotope systematic of bacterial formation and oxidation of methane. *Chem Geol*. **1999**. *161*, 291-314.

- A thorough review of the use of stable isotopes for distinguishing the origin of methane gas

Prinzhofer, A. & Pernaton, E. Isotopically light methane in natural gas: bacterial imprint or diffusive fractionation. *Chem Geol*. **1997**. *142*, 193-200.

- Bacteriogenic vs thermogenic CH₄: presents a method for graphing $\delta^{13}\text{C}$ of CH₄ vs C₂/C₁ ratio for distinguishing between fractionation of CH₄ as a result of mixing with bacteriogenic sources, and diffusive migration. This approach requires quantifying ethane, and potentially benefits greatly from

larger sample sizes. It is also greatly dependent on values chosen for diffusivities of the various gases ($^{12}\text{CH}_4$, $^{13}\text{CH}_4$, and C_2H_6) through their respective sediments. For this, a knowledge of the overlying geology, along with diffusivity estimates, is likely crucial.

Chung, H.M.; Gormly, J.R.; Squires, R.M. Origin of gaseous hydrocarbons in subsurface environments. *Chem Geol.* **1988.** *71*, 97-103.

- Thermogenic CH_4 – formation vs formation: For pure, unaltered thermogenic gas, a plot of inverse carbon order ($1/n$) against $\delta^{13}\text{C}$ can potentially be used to distinguish gases of different formations. This is because each formation may have distinct $\delta^{13}\text{C}$ associated with its parent material. For this analysis to work, $\delta^{13}\text{C}$ data is needed from higher C compounds such as ethane, propane, butane, and pentane.

- Bacteriogenic vs thermogenic CH_4 : As in the above diagnosis between thermogenic gases originating from different formations, the same graph may be used to spot mixing of thermogenic and bacteriogenic methane gases. Here, the linear slope of higher C compounds can be determined first. Then, the measured $\delta^{13}\text{C}$ of methane can be plotted and examined for fit. CH_4 fractionation that differs significantly from the line established by higher order C compounds indicates the presence and rough quantity of mixing. For this technique, the C_2+ $\delta^{13}\text{C}$ signature of the parent formation is needed. If C_2+ compounds are derived from a mixture of sources, a linear relationship cannot be established (See Figure 6).

** Whiticar, M.J.; Faber, E.; Schoell, M. Biogenic methane formation in marine and freshwater environments: CO_2 reduction vs. acetate fermentation – isotope evidence. *Geochim Cosmochi Ac.* **1986.** *50*, 693-709.

- Bacteriogenic CH_4 – freshwater vs marine origins: A clear method of delineation is established using the ratio of δD in H_2O and CH_4 plotted against the ratio of $\delta^{13}\text{C}$ in CO_2 and CH_4 .

Hewitt, J.L. The Levant investigation: using radiocarbon dating to determine the source of methane gas contamination. NYSDEC Division of Solid and Hazardous Waste. **1986.**

<http://info.ngwa.org/gwol/pdf/870143442.PDF>

- Demonstrates the use of radiocarbon dating as a technique for broadly constraining potential origins of gas contamination in Western NY

Harrison, S.S. Contamination of Aquifers by Overpressuring the Annulus of Oil and Gas Wells. *Ground Water.* **1985.** *23*, 317-324.

<http://onlinelibrary.wiley.com/doi/10.1111/j.1745-6584.1985.tb00775.x/abstract>

- Explains the danger that pressure build up within the well annulus can pose to ground water resources

Harrison, S.S. Evaluating system for ground-water contamination hazards due to gas-well drilling on the glaciated Appalachian plateau. *Ground Water*. **1983**. 21(6), 689-700.

<http://onlinelibrary.wiley.com/doi/10.1111/j.1745-6584.1983.tb01940.x/abstract>

- Provides a nice, though somewhat outdated, assessment of gas well drilling related hazards to ground, surface, and well waters using specific knowledge of geology in northwest PA

Schoell, M. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochim Cosmochi Ac.* **1980**. 44, 649-661.

- Bacteriogenic CH₄ – freshwater vs marine origins: For pure, unaltered bacteriogenic gas, a rough boundary may be drawn between freshwater (more positive) and marine (more negative) origins using a $\delta^{13}\text{C}$ value of -60‰. CH₄ (using both D and ¹³C fractionation ratios), along with isotopic analysis of CO₂ has been used to distinguish more distinctly between these types

USGS Stray Gas Workshop, Pittsburgh, PA (2009)

http://pa.water.usgs.gov/projects/energy/stray_gas/index.php

Texas A&M Stable Isotope Geosciences Facility

<http://stableisotope.tamu.edu/research-and-education/stable-isotope-principles>

NOAA Earth System Research Laboratory

<http://www.esrl.noaa.gov/gmd/outreach/isotopes/stable.html>