A Geochemical Context for Stray Gas Investigations in the Northern Appalachian Basin: Implications of Analyses of Natural Gases from Quaternary-through-Devonian-Age Strata in North-Central Pennsylvania

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Methane in the shallow subsurface as a dissolved gas in groundwater or in the gas phase is not unusual in aquifer systems above coal or petroliferous basins.

The origin may be:
* natural condition,
* result of legacy conditions,
* due to recent activity

Alleged stray gas migration incidents require investigation at the site specific level to determine origin and source. Conclusions must be supported by multiple lines of evidence.
Stray Gas Incidents

In general, we can categorize incidents as:

1) Non-threatening

2) Initially as non-threatening and escalate to potentially threatening

3) Threatening or catastrophic...
Investigations often reveal multiple potential stray gas sources.

- Natural condition in the aquifer
- Operating gas well
- Pipeline
- Underground coal mining

All incidents pre-date contemporary shale gas development.
Gas migration occurs from areas of high pressure to areas of lower pressure…

…water supply wells and buildings represent areas of lower pressure
~6 atm. → 1 atm. ~163 mg/l CH₄ can theoretically evolve from water

Max. CH₄ solubility @ 1 atm. = ~28 mg/l

Max. CH₄ solubility @ 6 atm. = ~193 mg/l

~ 6 atm.
Potential Mechanisms (typically) of gas migration if gas well related

- ineffective/poor cement
- fracture apertures increase
- no cement
- non-commercial gas charged zone

Modified after Harper 2012
In response to stray gas migration incidents in Pennsylvania, the Pennsylvania Oil & Gas regulations were revised & implemented on 2/5/2011:

§ 78.89. Gas migration response.

(a) When an operator or owner is notified of or otherwise made aware of a potential natural gas migration incident, the operator shall immediately conduct an investigation of the incident. The purpose of the investigation is to determine the nature of the incident, assess the potential for hazards to public health and safety, and mitigate any hazard posed by the concentrations of stray natural gas.

(b) The investigation undertaken by the operator under subsection (a) must include, but not be limited to, the following:

(1) A site visit and interview with the complainant to obtain information about the complaint and to assess the reported natural gas migration incident.

(2) A field survey to assess the presence and concentrations of natural gas and aerial extent of the stray natural gas.

(3) If necessary, establishment of monitoring locations at potential sources, in potentially impacted structures, and the subsurface.
(c) If combustible gas is detected inside a building or structure at concentrations equal to or greater than 10% (0.5% methane) of the L.E.L., the operator shall do the following:

(1) Immediately notify the Department, local emergency response agency, gas and electric utility companies, police and fire departments and, in conjunction with the Department and local emergency response agencies, take measures necessary to ensure public health and safety.

(2) Initiate mitigation measures necessary to control and prevent further migration.

(3) Implement the additional investigation and mitigation measures as provided in subsection (e)(1)—(5).
(d) The operator shall notify the Department and, in conjunction with the Department, take measures necessary to ensure public health and safety, if sustained detectable concentrations of combustible gas satisfy any of the following:

(1) Greater than 1% (0.05%) and less than 10% (0.5%) of the L.E.L., in a building or structure.

(2) Equal to or greater than 25% (1.25%) of the L.E.L. in a water well head space.

(3) Detectable in the soils (500 ppm proposed).

(4) Equal to or greater than 7 mg/l dissolved methane in water.
Various researchers have determined by examination of stable hydrogen and carbon isotopes of methane and C2+ hydrocarbons that there are common hydrogen and carbon isotopic compositions for thermogenic gas associated with coal and natural gas, drift gas, and other near-surface microbial gases (Craig, 1953; Coleman and others, 1977; Deines, 1980; Schoell, 1980; Rice and Claypool, 1981; Schoell, 1983; Whiticar, 1986; Wiese and Kvenvolden, 1993; Coleman, 1994; Baldassare and Laughrey, 1997; Kaplan and others, 1997; and Rowe and Muehlenbachs, 1999, Osborn and McIntosh, 2010).

The isotopic and compositional variations in natural gas can be described in terms of:

1) processes during the formation of gases (bacterial fermentation, maturation of organic matter) and
2) processes during secondary migration (mixing of primary gases).

The carbon and hydrogen isotopic compositional ranges of methane from different sources are based on the genetic classification scheme of Schoell (1980).

Stable carbon & hydrogen isotope compositions are expressed as the ratio of $^{12}$C to $^{13}$C and $^2$H/$^1$H of the sample compared with that of the international standards...expressed in the following notation as per mil.

$$ \delta R_x(\text{‰}) = \left( \frac{R_a / R_b \text{ sample}}{R_a / R_b \text{ standard}} - 1 \right) \times 10^3 $$

- International standards:
  - carbon: Pee Dee Belemnite (“PDB”)
  - hydrogen: Standard Mean Ocean Water (“SMOW”)

Properly interpreted, isotope geochemistry provides powerful geochemical evidence to constrain gas origin, and focus the investigation.
Sedimentary Organic Matter

\[ \text{CH}_3 \text{CO}_2 \]

Decarboxylation

Fermentation

\[ \text{CH}_4 \]

\[ \text{CO}_2 \]

Fermentation

Methyl Conversion

\[ \text{CH}_4 \]

Decarboxylation

Fermentation

\[ \text{CO}_2 \]

Reduction

\[ \text{HCO}_3^- \]

Other HCO_3- Sources

Sulfate-Reduction Zone

Sulfate-Free Zone

Anoxic environment necessary for microbial methane production

Modified from Whiticar et al., 1986

Microbial Methane
Acetate fermentation & CO_2 reduction methanogenesis pathways
+ early thermogenic oil associated thermogenic gas

Primary Stages of Hydrocarbon Generation

Marcellus (SW PA)

Marcellus (NE-NC PA)
Study Objective: determine the occurrence and identify the origin of natural gases in Quaternary through Devonian age strata within our study area in the N. Appalachian basin...this objective was accomplished comprehensively by evaluating different data types:

1) Molecular & Isotopic compositions for > 1,900 gas samples obtained during drilling of contemporary Marcellus formation gas wells

2) Historical evidence including gas shows documented in well completion reports and well records on file with PA Geological Survey & published data from previous investigations

3) Molecular & Methane Isotopic compositions for background groundwater water quality of local and regional aquifer systems
Five County Study Area
In N.E. Pennsylvania
Mudgas Isotope Geochemistry

Our database for this study includes 2,274 gas samples analyzed & interpreted for molecular & isotopic composition from 234 Marcellus Fm. gas wells

Isotope analyses for mudgases are accomplished using online continuous flow, or GC-IRMS systems with a precision of +/- 0.3 to 0.4 on 13C and +/- 5 for 2H

When combined with geographic and stratigraphic data, the mudgas isotope data provide important depth specific background isotope compositions of gases that occur in the strata which can be diagnostic for investigations of potential stray gas migration incidents.
Shallow gas shows encountered in aquifer system during drilling of Marcellus Fm. wells. Gases are thermogenic in origin.
Shallow gas shows encountered in aquifer system during drilling of Marcellus fm. Wells. Gases are thermogenic in origin.
Shallow gas shows encountered in aquifer system during drilling of Marcellus fm. wells

Gases are thermogenic in origin

Partial isotope reversal at 354’ BGS
Isotope Crossplot
Catskill & Lock Haven Fms. vs Tully Fm., Hamilton Gp. & Marcellus Fm.

δD of Methane

δ13C of Methane

Sub-Surface Microbial Gas
(CO₂ Reduction)

Thermogenic Gas
("Natural Gas" and Coal Gas)

Near-Surface Microbial Gas
(Fermentation)

Catsskill & Lock Haven Fms. × Marcellus Fm. ♦ Hamilton Group ○ Tully Fm.

δ13C1 vs. δ13C2 MGL Isotope compositions for gas in the Catskill & Lock Haven Formations & the Tully Fm., Hamilton Group, and Marcellus Fm. (Modified after Coleman, 1993)
MGL Isotope data reveal thermogenic gases occur in the aquifer system distinct from deeper gases & Marcellus Fm. gas.
All gases within the study area are dry with minor C2+ concentrations.
Partial isotope reversals observed universally in Marcellus Fm.
Marcellus fm. gas well
Bradford County, PA

- Partial isotope reversals documented in shallow system
- Shallow thermogenic gas throughout sample interval
- Seal?
- Partial isotope reversals documented in shallow system
Marcellus fm. gas well
Tioga County, PA

- Genetically distinct from gas below 5,700'. No isotope reversals, 1,748'-1,840' interval reveals reversal, however, within limit analytical precision.

- Seal/overpressure?

- Isotope reversals throughout 5,700'-6660' interval. Gas in this interval is genetically distinct from the gas above 5,700'.
Representative gas shows for Catskill/Lock Haven from completion reports of Upper Devonian & Marcellus wells

Catskill/Lock Haven is the aquifer system in many areas of NE. Pennsylvania

Source: well completion reports on file w/PA Geological Survey
Background δ13C1 and δD compositions for dissolved phase and gas phase methane (pre-contemporary Marcellus Fm. well drilling activity)
Our data reveals shallow microbial gas and mixed microbial/thermogenic gas in glacial drift/bedrock in the western part of our study area, and thermogenic gas of different thermal maturities in the aquifer system and shallow section of the Upper Devonian strata in the eastern part of our study area.

Distinct thermogenic gases evident throughout the Devonian system.

Contrary to geochemical modeling of Kinetic Isotope effects, in certain areas of the basin in NE PA, isotope data reveals partial reversals (\(\delta^{13}C_1 > \delta^{13}C_2\)) throughout the section, & universally in the Marcellus formation.

The origin of reversals in shale gas plays is the subject of recent debate & research where mixing, closed system shale with heating of kerogen, and oil & gas, and Rayleigh-type fractionation of isotopic compositions of C\(_2\), C\(_3\), & late stage generation of methane during maximum burial have been recently advanced. (Burruss, Laughrey, 2010, Tilley et. al., 2011, Xia, et.al., 2012, in press)
Thank you

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