

Rocky Mountain EHS Peer Group

## Understanding Chemical and Isotopic Fingerprinting in Colorado's Oil and Gas Regulations

Patrick Travers Q1 2023 RMEHSPG Meeting 1/19/2023





Image courtesy of University of Queensland Stable Isotope Geochemistry Laboratory

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PDT Engineering, LLC



- Chemical/isotopic sample data integration and interpretation
- Hydrocarbon source forensic investigations
- Navigating COGCC regulations requiring chemical and isotopic sample analysis

## Colorado's Sample Dataset is Unique

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- 2005: COGCC groundwater sampling in GWA (Greater Wattenberg Area) for infill wells
- 2009: COGCC COA's can require groundwater sampling
- 2007: COGCC/ LTE GWA Baseline Study
- 2011: COGA Voluntary Baseline Groundwater Monitoring Program
- 2013: CO first state to require statewide baseline and post-drill groundwater sampling
- 2017: Bradenhead Testing Guidance (included sampling)
- 2019: COGCC Order 1-232 Bradenhead Monitoring and Testing Area (GWA)
- 2020: SB 181
  - Rule 615: Groundwater Baseline Sampling and Monitoring
  - Rule 419: Bradenhead Monitoring, Testing and Reporting



Images from COGCC GIS Online, 2023



# Colorado's Chemical and Isotopic Datasets

Two main types of sample data:

- <u>Groundwater Monitoring</u>

   a) Initial Rule 615 analytical suite
   If those results > 1.0 mg/l
   dissolved gas threshold, then
   b) Gas composition analysis
   c) Stable isotope analysis
- 2. <u>Bradenhead Monitoring</u>

Analysis determined by sample matrix (oil, gas, water)



Gas Composition Analysis **PDT ENGINEERING** 



GC schematic courtesy of Thomas Warwick



Gas Chromatogram output of a typical natural gas sample run on Agilent's Natural Gas Analyzer GC

# Stable Isotope Analysis



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Carbon-12: 6 protons, 6 neutrons ~ 99% natural abundance Carbon-13: 6 protons, 7 neutrons ~ 1% natural abundance



Schematic of magnetic sector Isotope Ratio Mass Spectrometer (IRMS) used to measure stable carbon isotope ratios. Courtesy of Carleton College.

> Mass 44: <sup>12</sup>C<sup>16</sup>O<sup>16</sup>O Mass 45: <sup>13</sup>C<sup>16</sup>O<sup>16</sup>O Mass 46: <sup>12</sup>C<sup>16</sup>O<sup>18</sup>O





Manny Ramirez returning to baseball as an Albuquerque Isotope after a 50-game ban, triggered by carbon isotope testing for synthetic testosterone.



### Natural Gas Origin



### Methane (CH<sub>4</sub>)

Stable isotopes <sup>13</sup>C/<sup>12</sup>C and <sup>2</sup>H/<sup>1</sup>H can be measured in methane, ethane, propane, etc.

#### Microbial (biogenic) Gas

- Isotopically depleted in <sup>13</sup>C, <sup>2</sup>H
  - $\delta^{13}CC_1 < -60\%$
- Primarily methane
  - < 1% C<sub>2</sub>+
- Formed by bacterial processes, i.e. fermentation or CO<sub>2</sub> reduction
- Fermentation occurs naturally in near-surface freshwater environments (compost, landfills, sewers, swamps, etc.)
- Not typically associated with oil and gas development

#### **Thermogenic Gas**

- Isotopically enriched in <sup>13</sup>C, <sup>2</sup>H
  - $\delta^{13}CC_1 > -55\%$
- Significant quantities of C<sub>2</sub>+
- Formed by the thermal breakdown of buried organic material
- Requires extreme heat and pressure in the subsurface over geologic timeframes
- Formed naturally with the generation of petroleum in the subsurface
- Can be associated with oil and gas development

Determination of microbial vs thermogenic gas source is required when COGCC baseline samples > 1.0 mg/l dissolved gas.

### Not New Analytical Techniques **PDT ENGINEERING**

#### Original script written by Horace Greele Weekly Tribune established 1870 GREELEY, COLORADO 80631 VOL. 76, NO. 140 La Salle: Gas threat spreads rouncing of Walter Mondale in Vermont is fresh evidence the Democratic primary tide is turning in his favor, but contends his campaign will "still be playing catch-up" at least through the month Out at dawn, the Colorado senator greeted workers at a Birmingham, Ala., plant with "I'm Gary Hart, running for president. I need your help." Interviewed on the NRC-TY Today" show, Hart said Tuesday's victory in the non-binding Vermont primary "continues very much what seems to be pattern evolving." He added, "There have been three states in a row ... that seem to be moving in our direction." Yet, with Mondale's campaign outspending his 10-to-1, Hart said "In many respects, I guess, I'm still the underdog ... I think we'll still be playing catch-up, if you

Public Works Director Doyle Schaeffer monitors gas leak Tuesday in hole dug near United Bank of La Salle Schools hank close nrohe intensifies

WEDNESDAY, MARCH 7, 1984 25 CENTS Hart captures Vermont, sees tough month the former vice president in Gary Hart said today his 3-1 plored: "This is not just a horse race. This has become a battle for the soul of the Democratic Party and the future of our country It is a horse race that has see Hart win an ever-increasing share of the votes: 37 percent to Mondale's 28 percent in New Hampshire; 51 percent to 44 percent in Maine; and 71 percent to 20 percent in Vermont Mondale, once the front-rupner and the victor so far in only the Iowa party cancuses, looked south his comeback, campaigning today in Georgia, Alabama and Florida - three of the nine states holding Democratic presidential primaries and caucuses on Super Tuesday" next week Cheering the Vermont results Hart campaign manager Oliver

Henkel proclaimed:

defeat Ronald Reagan

"If I were in the White House

would be very concerned about

the Hart candidacy. He represents a far more significant threat will, throughout the rest of this to the president than does Walter month at least In Washington, House Speaker And Hart, noting indications of " Thomas P. O'Neill Jr. said today a Republican cross-over vote in that Hart is now clearly the Vermont, declared, "I intend to

front-runner and that Mondale

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- Feb. 18, 1984: Lumberyard explosion in La Salle, CO
- Abandoned water well venting gas into showroom. 5 abandoned water wells in area with gas (240-335 m)
- Gas source/ origin?



- USGS -> 1) gas composition and 2) stable isotope analysis
- Gas was thermogenic, originating from Codell formation (~7,000 ft)
- Specific migration pathway not determined

1/19/23







# Denver Basin Baseline Groundwater Dataset



### Groundwater methane in relation to oil and gas development and shallow coal seams in the Denver-Julesburg Basin of Colorado

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Edited by Peter H. Gleick, Pacific Institute for Studies in Development, Environment, and Security, Oakland, CA, and approved June 7, 2016 (received for review November 24, 2015)



#### From Sherwood et al. (2016)

### Sherwood et al. (2016) Groundwater Data



n=924 groundwater wells sampled Methane detected in n=593 wells, n=261 methane > 1 mg/ln=42 contained thermogenic or mixed biogenic/thermogenic methane (32 separate cases)

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# Sampling and Analysis for Wellbore Integrity

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- "Bradenhead" aka surface casing annulus
- Bradenhead pressure can have multiple sources and sustained pressure can be a wellbore integrity indicator
- Bradenhead pressure monitoring generally required monthly in CO and during HF
- Bradenhead tests (Form 17) required annually on all CO wells
- Samples can be collected during testing (oil, gas, water) for diagnostic testing



Illustration courtesy of Southwestern Energy

# Bradenhead Sampling and Analysis



Example wellbore schematic with potential bradenhead migration scenarios (Lackey, 2022)



- Lackey et al. (2022) compiled data from n=3,399 samples in COGCC database
- Testing requirements different for oils, gases, waters
- Analytical data can help to determine source of annular (bradenhead) pressure

### GWA Bradenhead Samples



■ Aqueous Liquid ■ Gas ■ Non-aqueous Liquid

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### 1) Bradenhead Gas Analysis

**COGCC** specifies:

- gas composition
- stable carbon ( $\delta^{13}$ C  $C_1 - C_5$  and  $CO_2$ ) and hydrogen ( $\delta D C_1$ ) isotope analysis

**Applications:** 

**Biogenic/**thermogenic Forensics (source)



casing and production gas samples (Lackey, 2022)

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COGCC specifies analysis of:

- major anions (Cl, CO<sub>3</sub>, HCO<sub>3</sub>, SO<sub>4</sub>)
- major cations (Na, K, Ca, Mg)
- TDS
- BTEX
- Dissolved Gases
- Diesel Range Organics (DRO)
- Gasoline Range Organics (GRO)



Applications:

- various formations in the Denver Basin (COGCC, 2022)
- Forensics, though more limited
- Determining petroleum content

Most aqueous bradenhead samples contain hydrocarbons. BTEX detected in 99.7% COGCC GWA bradenhead water samples per Lackey, 2022.

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# Groundwater Investigations/ Complaints



From Sherwood et al. (2016)

- Same analytical techniques are applied to complaints/ groundwater investigations
- Integrated with production and bradenhead gas sampling and pressure testing of nearby (< 1 mi) oil and gas wells</li>
- Dissolved gas in water well was isotopic match to J-Sand production (eliminated 6/11 nearby wells as potential culprits)
- High bradenhead pressure, short surface casing identified the culprit well
- Remediation caused a significant drop in gas flow rate from contaminated well



- CO regs and dataset are unique
  - n > 60,000 samples
- Chemical and/or isotopic analysis required by COGCC:
  - Groundwater monitoring
  - Bradenhead monitoring
- These data can be used for:
  - Microbial (biogenic) vs thermogenic gas origin
  - Determining source of annular fluids (oils, gases, waters)
  - Forensic Investigations



Image from COGCC GIS Online, 2023

### Additional Questions? Please Contact

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