Chemical and Isotopic Testing as Part of Colorado's Unique Approach to Monitoring Oil and Gas Development ***What Have We Learned?***

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ENVIRONMENTAL® STANDARDS
Montrose Environmental Group

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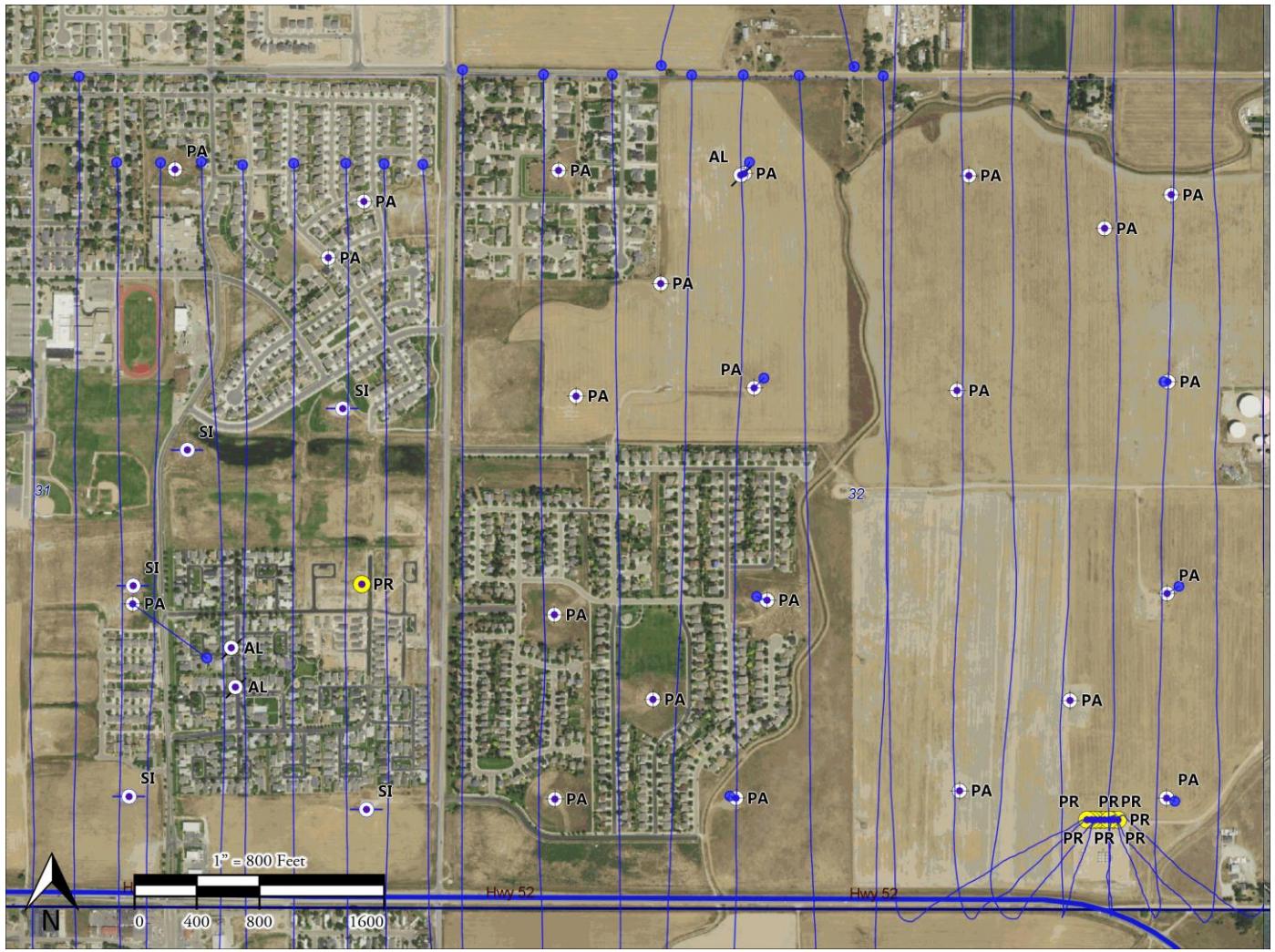
Introduction

- Colorado Oil and Gas Background
- Required Sampling and Analysis
  - Stable Isotope Analysis
- Applications
  - Determining Natural Gas Origin
  - Denver Basin Dissolved Methane Dataset
  - Stray Gas Forensic Investigations
  - Wellbore Integrity Monitoring
- Questions?

Image courtesy of University of Queensland Stable Isotope Geochemistry Laboratory

Study Location



Images from COGCC GIS Online, 2023

Colorado Regulations Timeline

- **2005**: COGCC groundwater sampling in GWA (Greater Wattenberg Area) for infill
- **2007**: COGCC/ LTE GWA Baseline Study
- **2009**: COGCC COA's can require groundwater sampling
- **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**: CO Senate Bill 181
  - Rule 615: Groundwater Baseline Sampling and Monitoring
  - Rule 419: Bradenhead Monitoring, Testing and Reporting

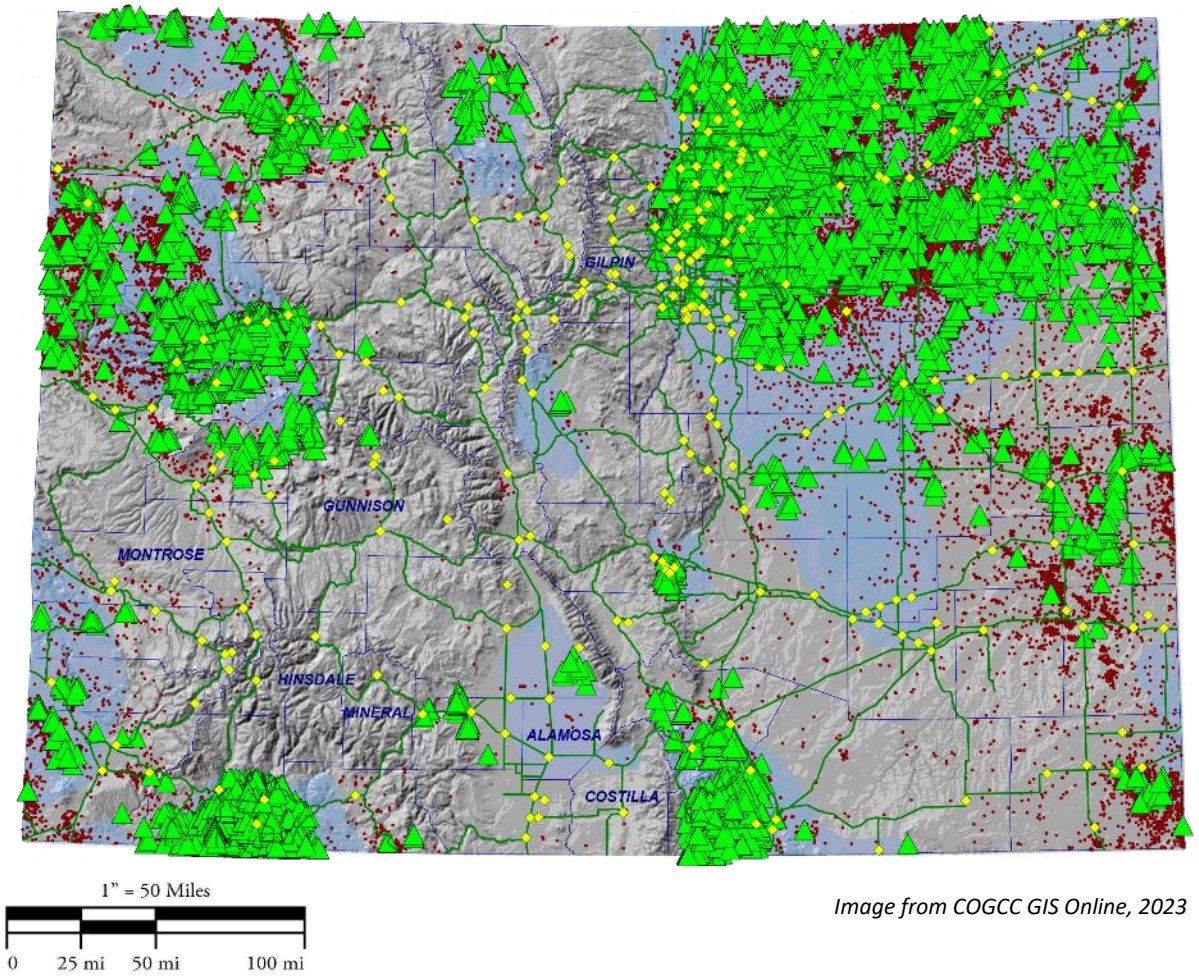


Image from COGCC GIS Online, 2023

What is a Bradenhead?

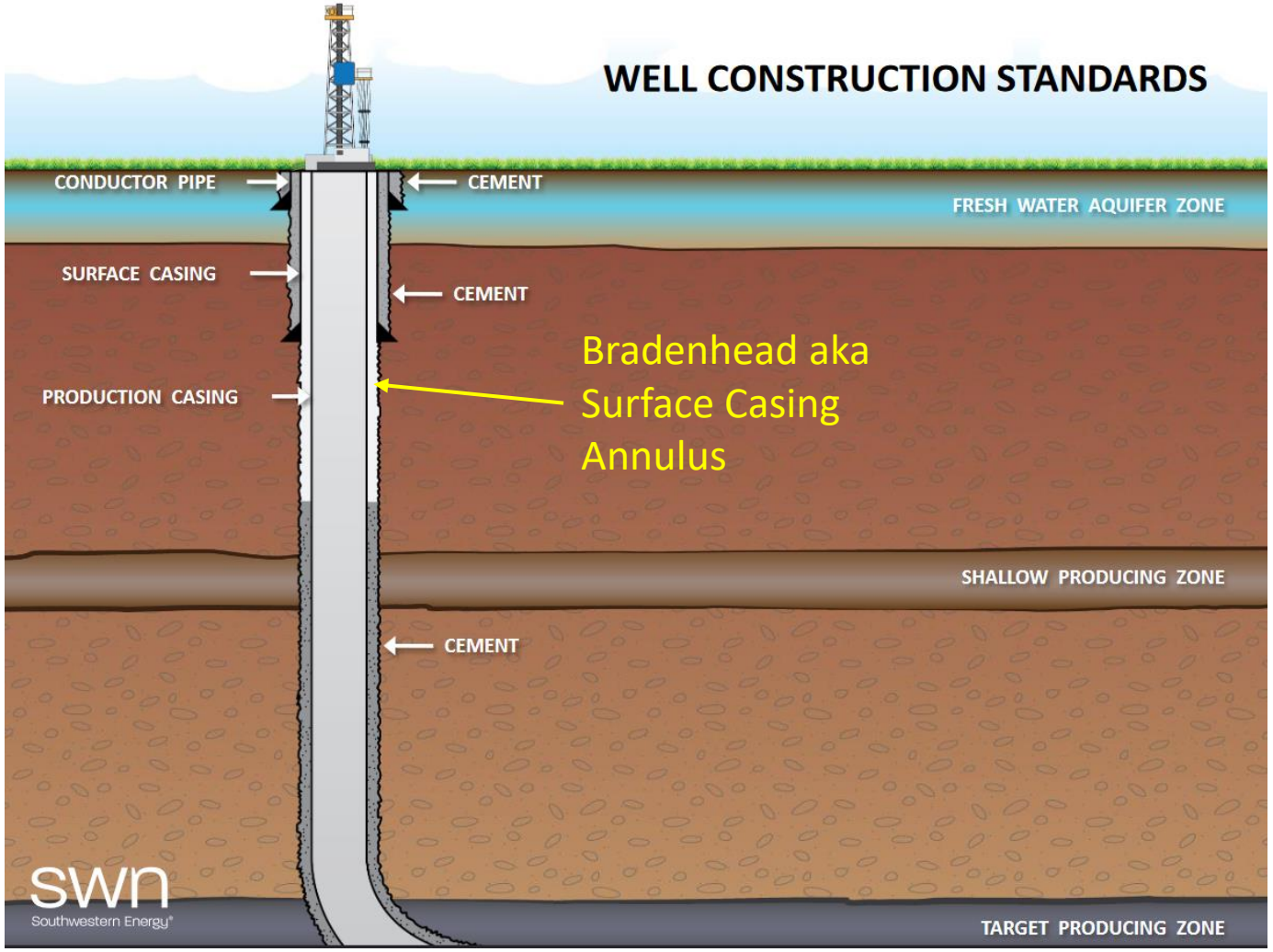


Illustration courtesy of Southwestern Energy

- Surface casing is an additional casing string isolating freshwater aquifers from wellbore
- Annulus between surface casing string and next smaller diameter casing string = “Bradenhead”
- Bradenhead monitoring, sampling and analysis is one way to evaluate and monitor wellbore integrity

Well-Established Analytical Techniques

GREELEY TRIBUNE

The Greeley Daily Tribune

Original script written by Horace Greeley — Weekly Tribune established 1870

VOL. 76, NO. 140 — GREELEY, COLORADO 80631 — WEDNESDAY, MARCH 7, 1984 — 25 CENTS

La Salle: Gas threat spreads

United Bank

Public Works Director Doyle Schaeffer monitors gas leak Tuesday in hole dug near United Bank of La Salle.

Tribune photo by Geoff Forester

Schools, bank close; probe intensifies

Hart captures Vermont, sees tough month

MONTPELIER, Vt. (AP) — Gary Hart said today his 3-1 trouncing 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 NBC-TV "Today" show, Hart said Tuesday's victory in the non-binding Vermont primary "continues very much what seems to be a pattern evolving."

He added, "There have ... three states in a row ... th... to be moving in our direc...

Yet, with Mondale's ... outspending his 10-to-1 ... "In many respects, I ... still the underdog ... I ... still be playing catch ... will, throughout the ... month at least."

In Washington, Hou... Thomas P. O'Neill Jr. ... that Hart is now ... front-runner and tha... will be able to overtak...

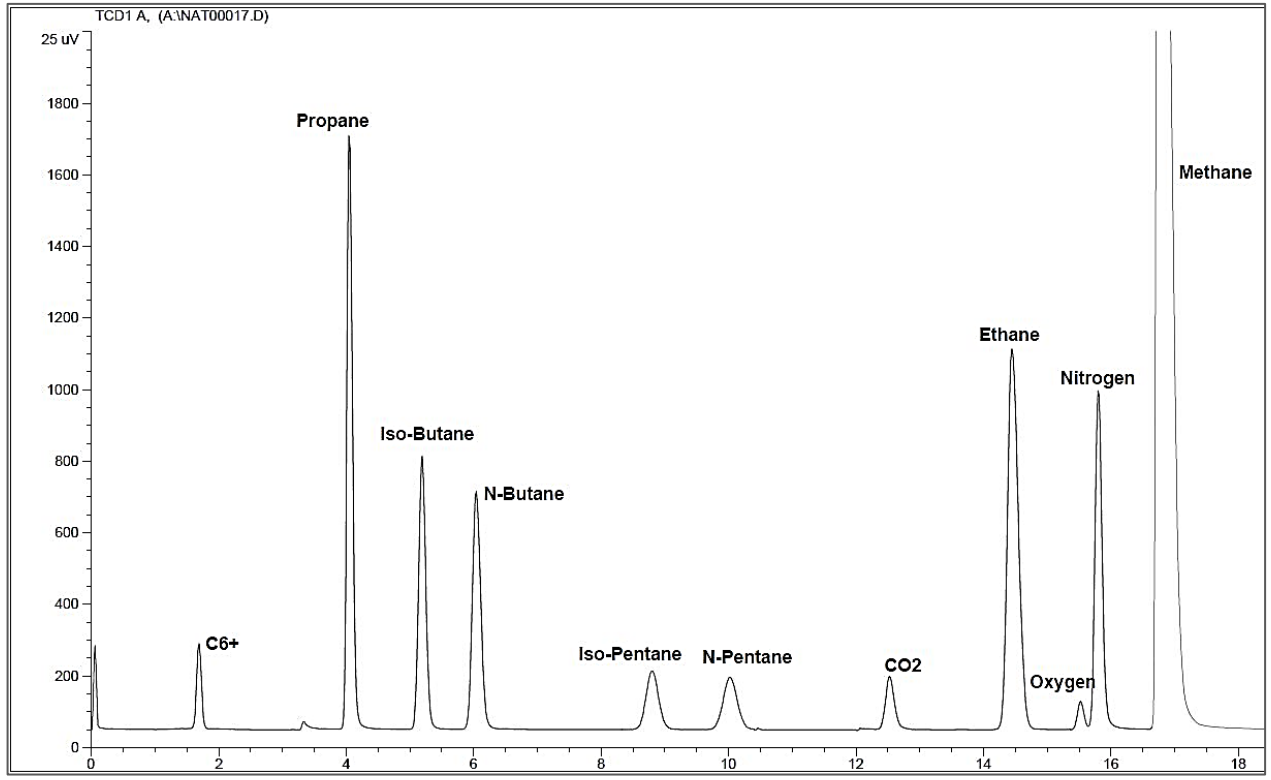
the former vice president implored: "This is not just a horse race. This has become a battle for the soul of the Democratic Party and the future of our country."

It is a horse race that has seen 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 29 percent in Vermont.

Mondale, once the front-runner and the victor so far in only the Iowa party caucuses, looked south for his comeback, campaigning today in Georgia, Alabama and Florida — three of the nine states holding Democratic presidential primaries and caucuses on

- Feb. 18, 1984: Lumberyard explosion in La Salle, CO
- Abandoned water well located under lumberyard
- Five additional abandoned water wells identified with gas
- USGS studied potential gas sources using gas composition and stable isotope analysis
- Gas originated from Codell formation (~7,000 ft), though specific migration pathway not determined

Current Sampling and Analysis Requirements



Gas chromatogram output of a natural gas reference sample analysis, courtesy of Agilent

Groundwater Monitoring

1. Initial analytical suite

   If CH_4 > 1.0mg/l, then:

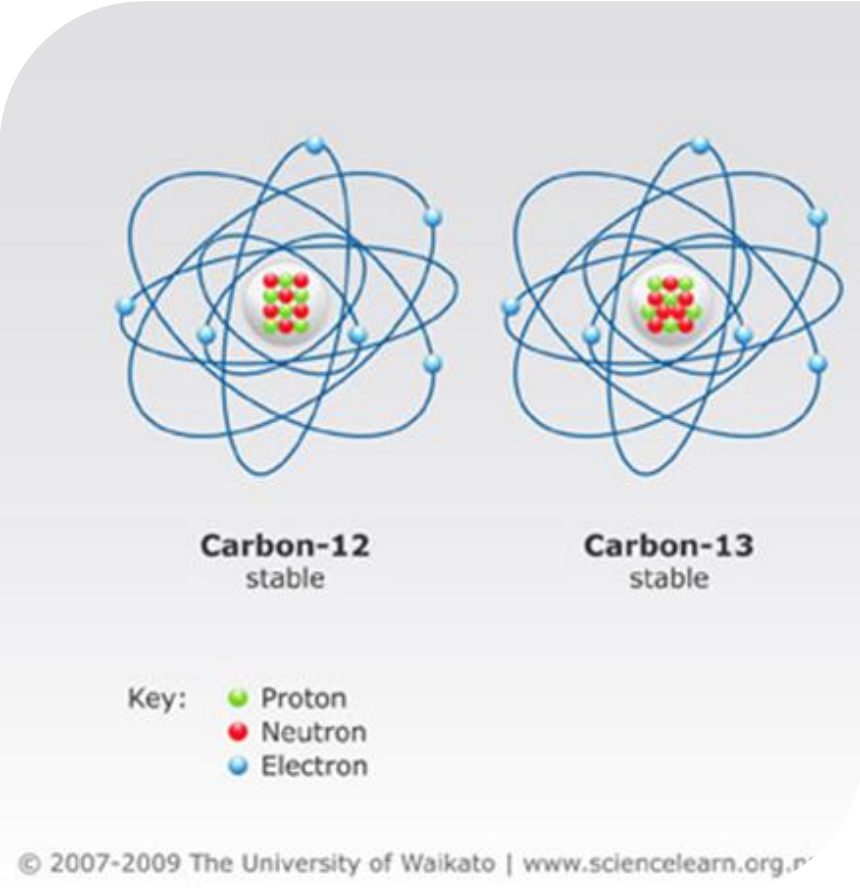
2. Gas composition analysis
3. Stable isotope analysis

Wellbore Integrity Monitoring

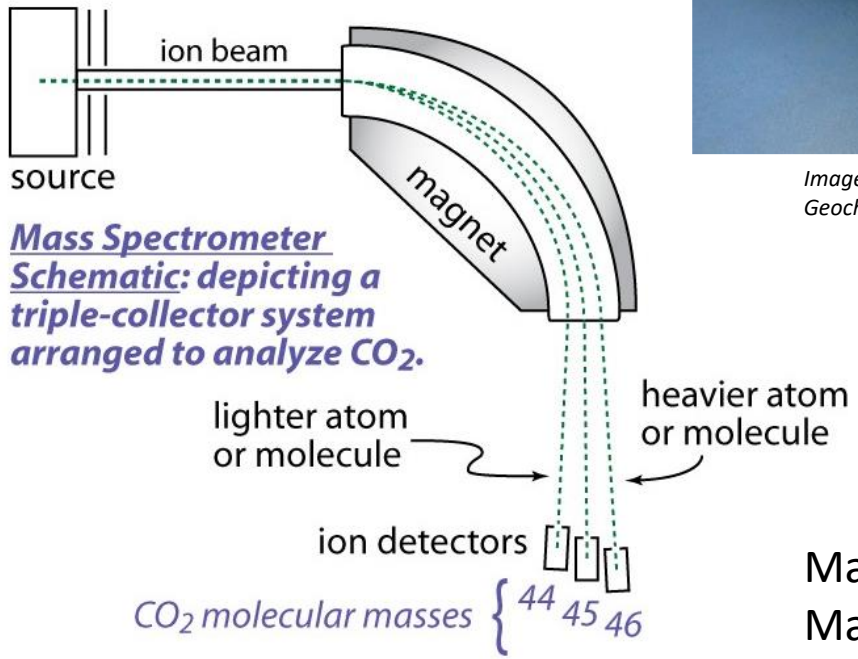
If surface casing annular pressure > threshold, then:

1. Gas composition and stable isotope analysis (gas)
2. TPH, TDS, major ions, etc. (water)
3. Whole oil analysis (non-aqueous liquids)

Stable Isotope Analysis



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

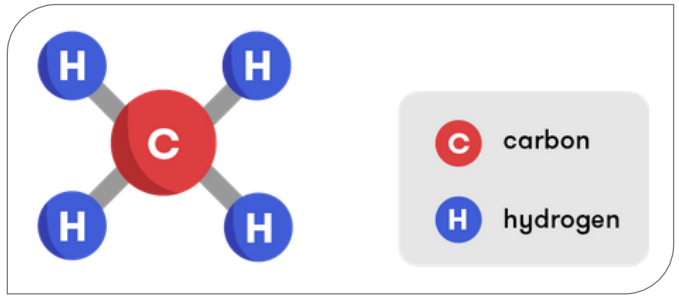


Schematic of magnetic sector Isotope Ratio Mass Spectrometer (IRMS) used to measure stable carbon isotope ratios. Courtesy of Carleton College.

Image courtesy of University of Queensland Stable Isotope Geochemistry Laboratory

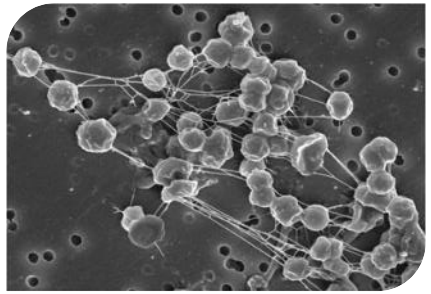
Mass 44: $C^{12}O^{16}O^{16}$
Mass 45: $C^{13}O^{16}O^{16}$
Mass 46: $C^{12}O^{16}O^{18}$

Determination of Natural Gas Origin



Methane (CH_4)

Stable isotopes C^{13}/C^{12} and H^2/H^1 are measured in methane, and can also be measured in ethane, propane, etc.



Microbial (biogenic) Gas

- Predominantly methane
- Isotopically ***depleted*** CH_4
- Formed by bacterial processes, i.e, fermentation or CO_2 reduction
- Fermentation often occurs naturally in near-surface freshwater environments

Thermogenic Gas

- Significant quantities of C_2+ present with methane
- Isotopically ***enriched*** CH_4
- Formed by the thermal breakdown of buried organic material under extreme heat and pressure over geologic timeframes

Natural Gas Origin Re-visited

Clip from Fox, Josh, et al. *Gasland: Can You Light Your Water On Fire?* New York, NY, Docurama Films, 2010.

Denver Basin Baseline Groundwater Dataset

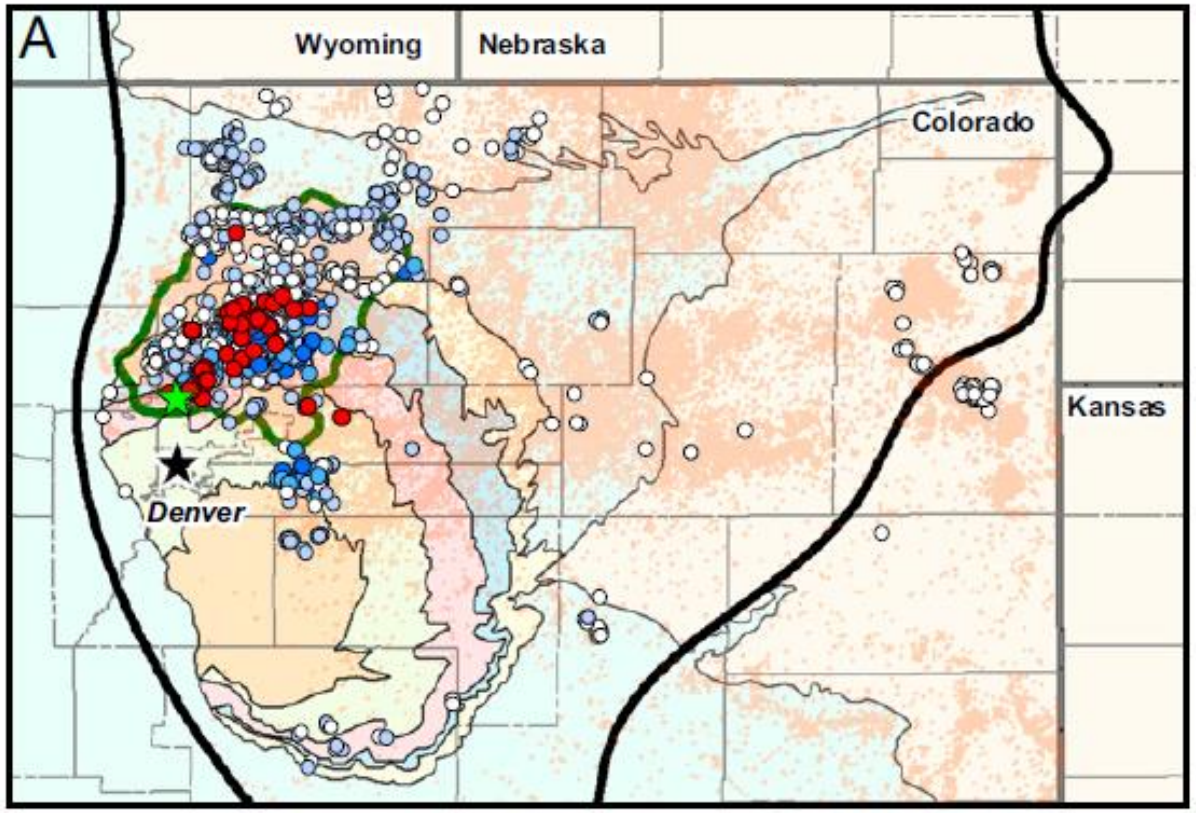
PNAS

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

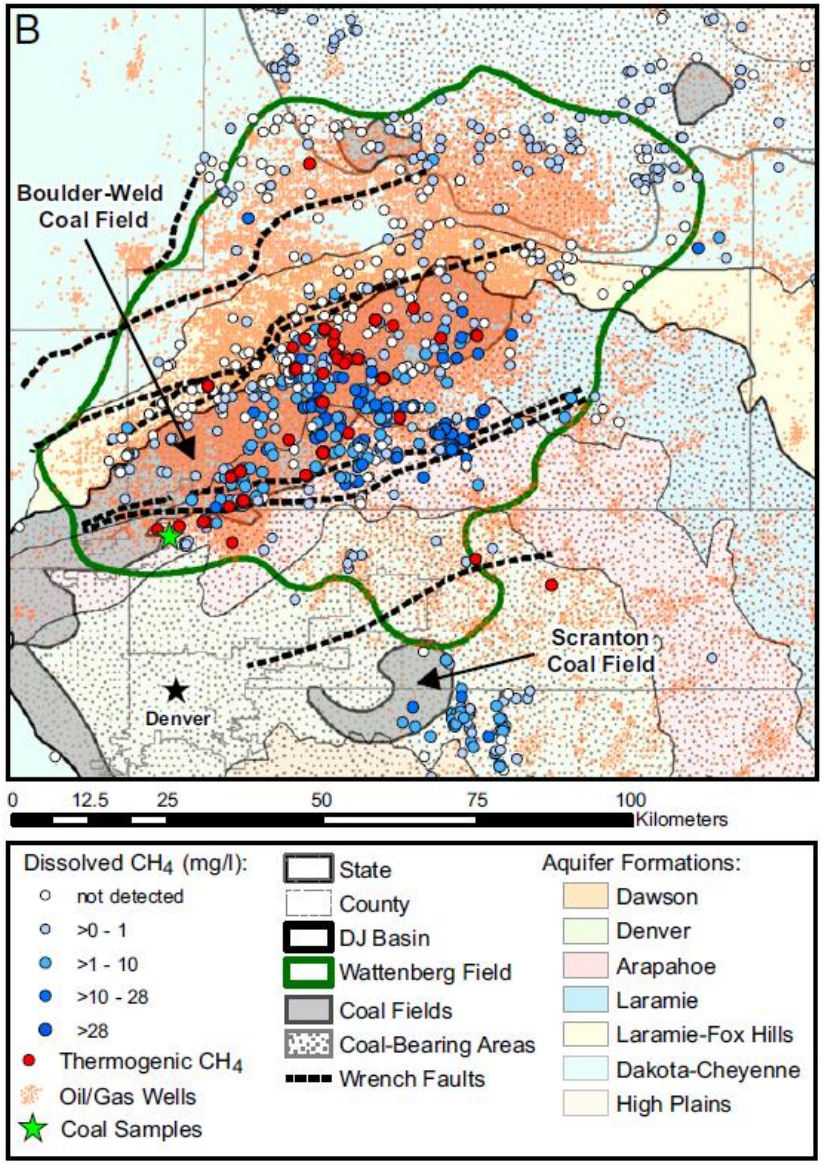
Owen A. Sherwood[a,1], Jessica D. Rogers[b], Greg Lackey[b], Troy L. Burke[b], Stephen G. Osborn[c], and Joseph N. Ryan[b]

[a]Institute of Arctic and Alpine Research, University of Colorado, Boulder, CO 80309; [b]Department of Civil, Environmental and Architectural Engineering, University of Colorado, Boulder, CO 80309; and [c]Department of Geological Sciences, California State Polytechnical University, Pomona, CA 91768

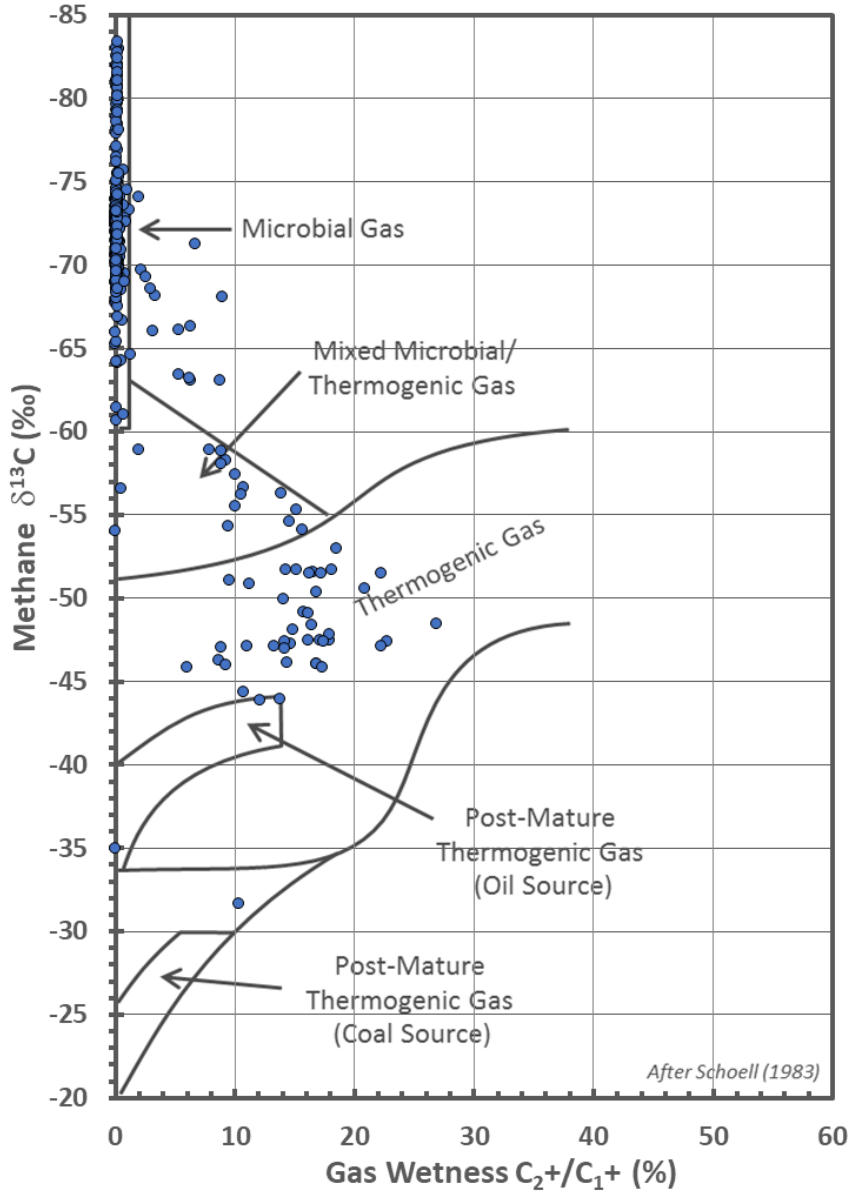
Edited by Peter H. Gleick, Pacific Institute for Studies in Development, Environment, and Security, Oakland, CA, and approved June 7, 2016 (received for review November 24, 2015)

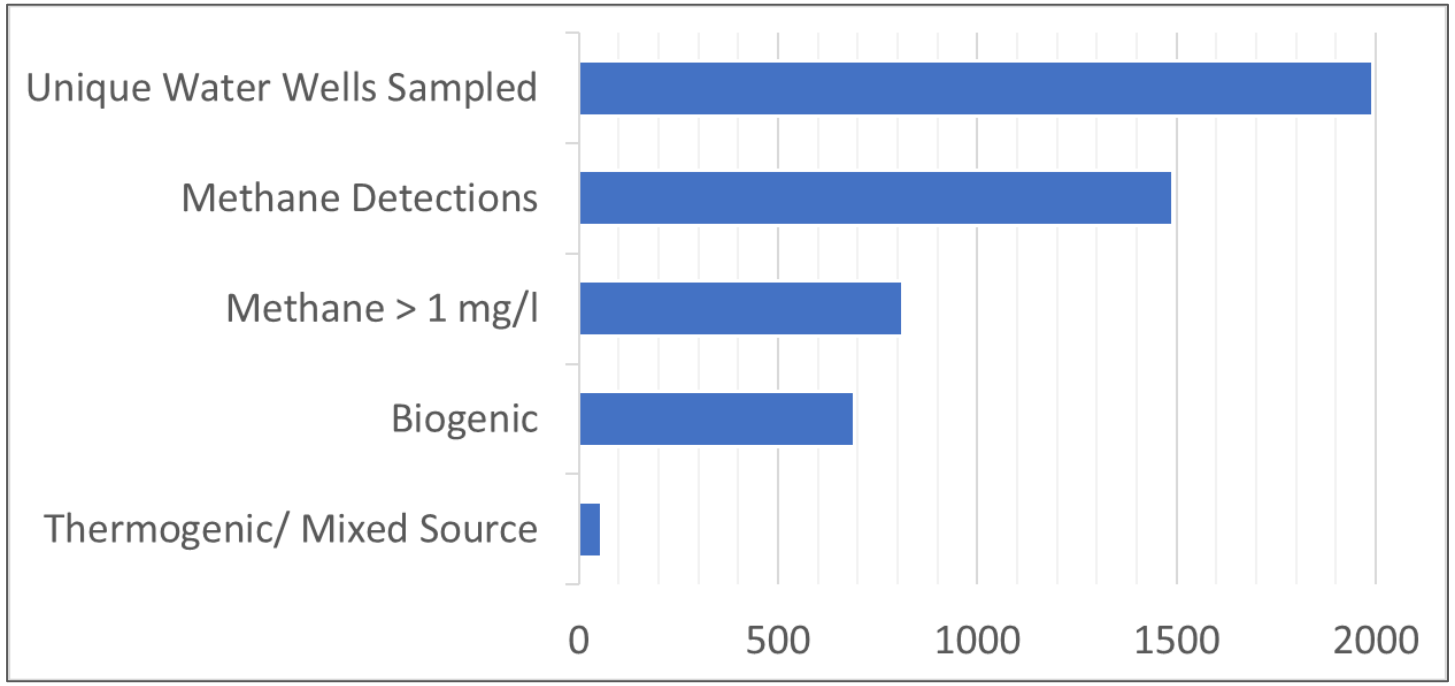


From Sherwood et al. (2016)



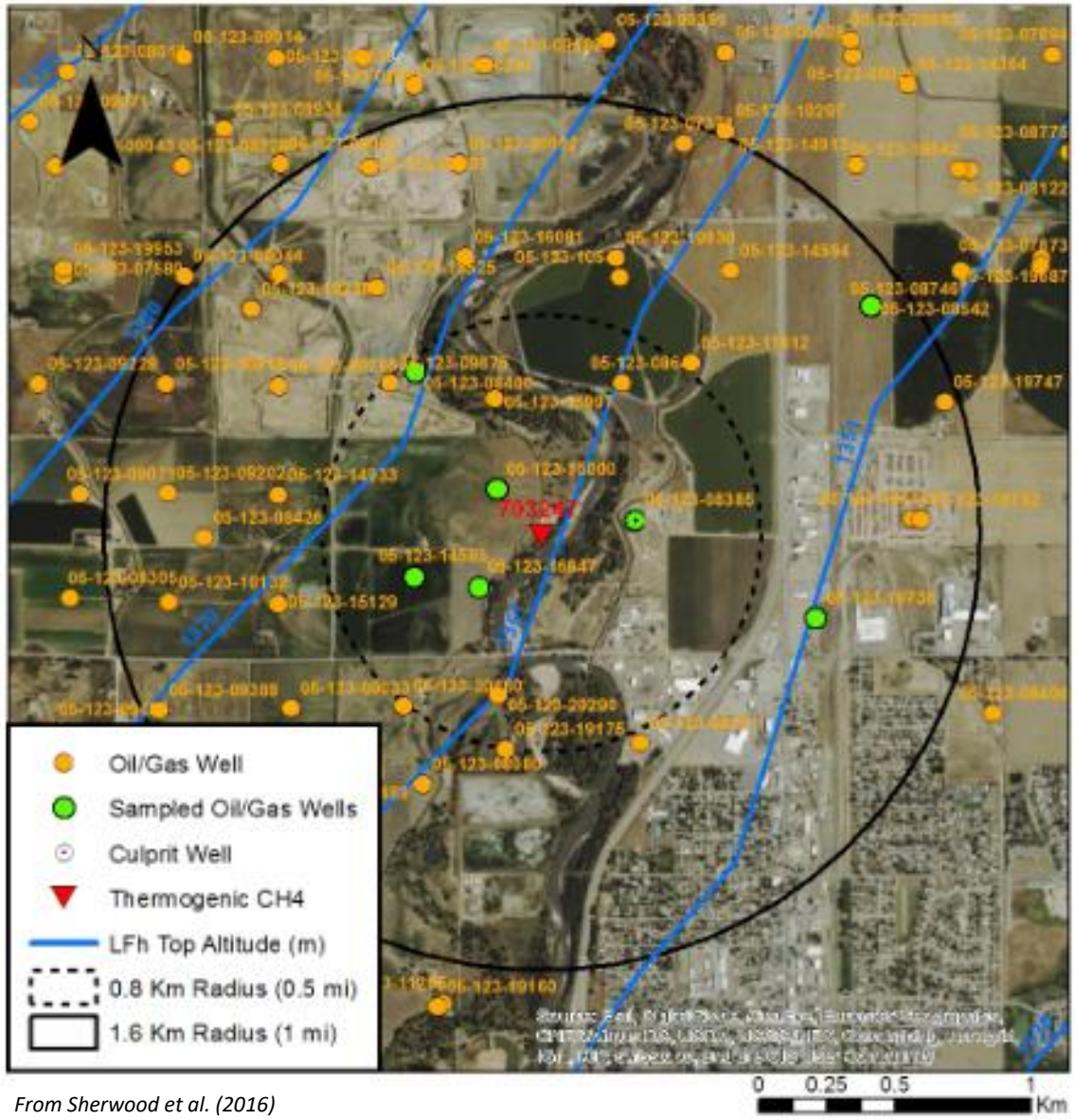
Denver Basin Baseline Groundwater Dataset (Update)





Data downloaded from the COGCC COGIS sample database, 2023.

Stray Gas Forensic Investigations



From Sherwood et al. (2016)

- Same analytical techniques are applied to forensic groundwater investigations
- Includes sampling and isotopic analysis integrated with C_1/C_2+ mixture data for nearby oil and gas wells for forensic comparison
- Dissolved gas in water well was isotopic match to specific formation
- Isotopic data, pressure monitoring and well construction records identified the source well
- Remediation caused a significant reduction in gas in contaminated well

Sampling and Analysis for Wellbore Integrity

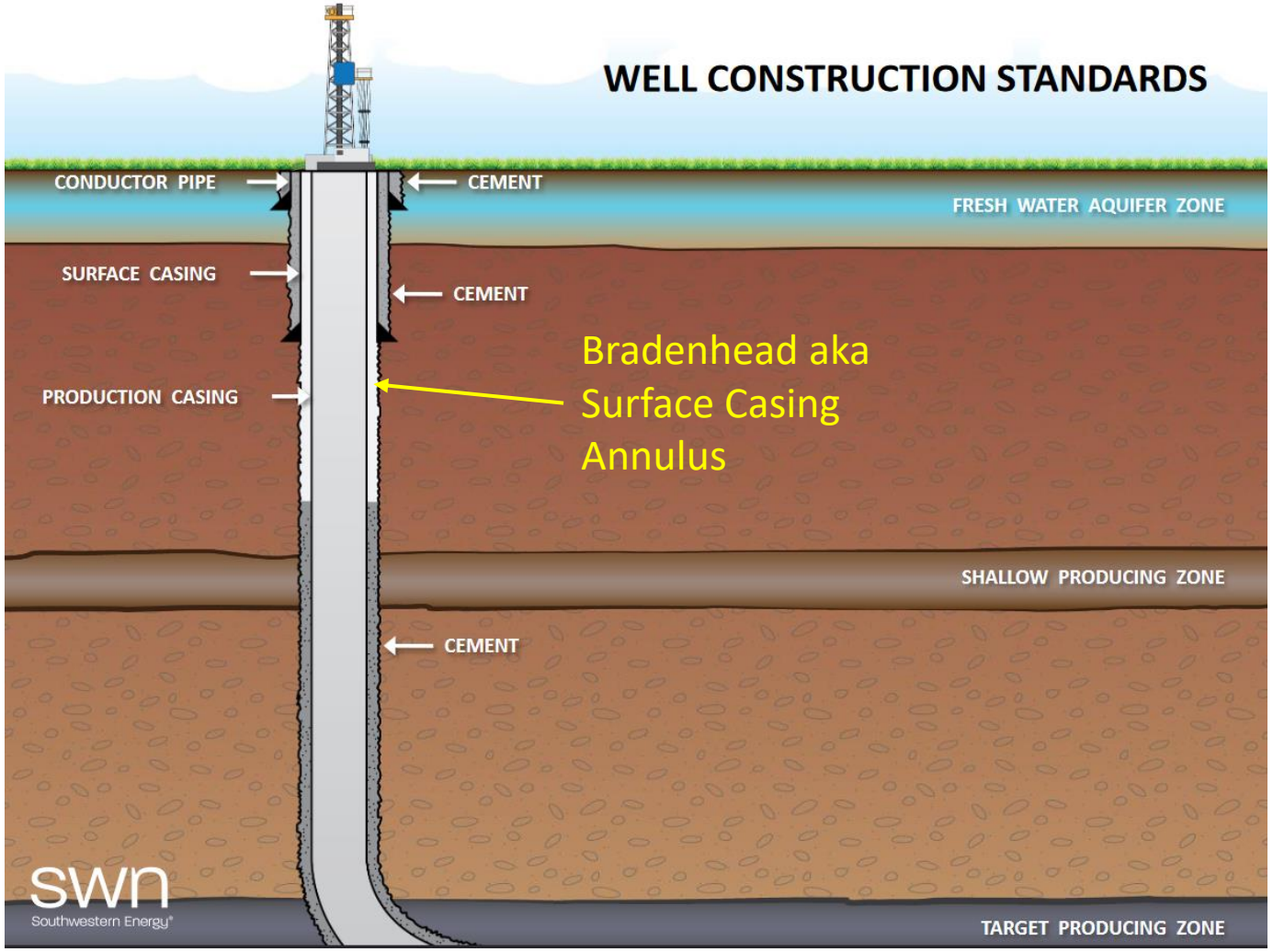
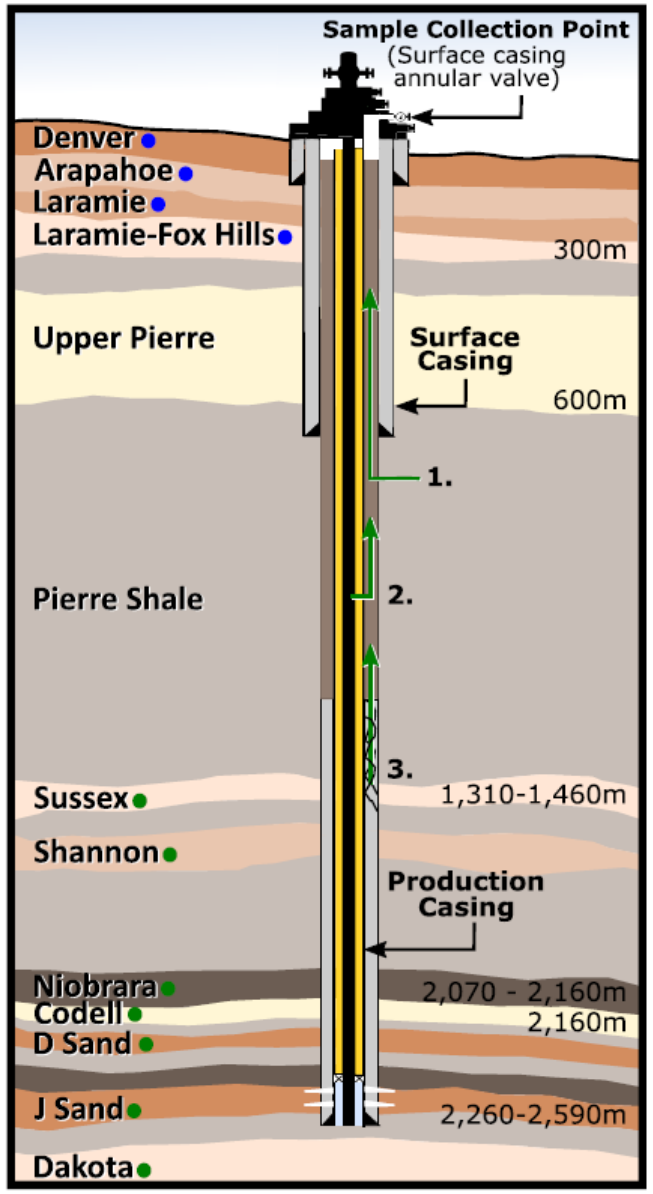


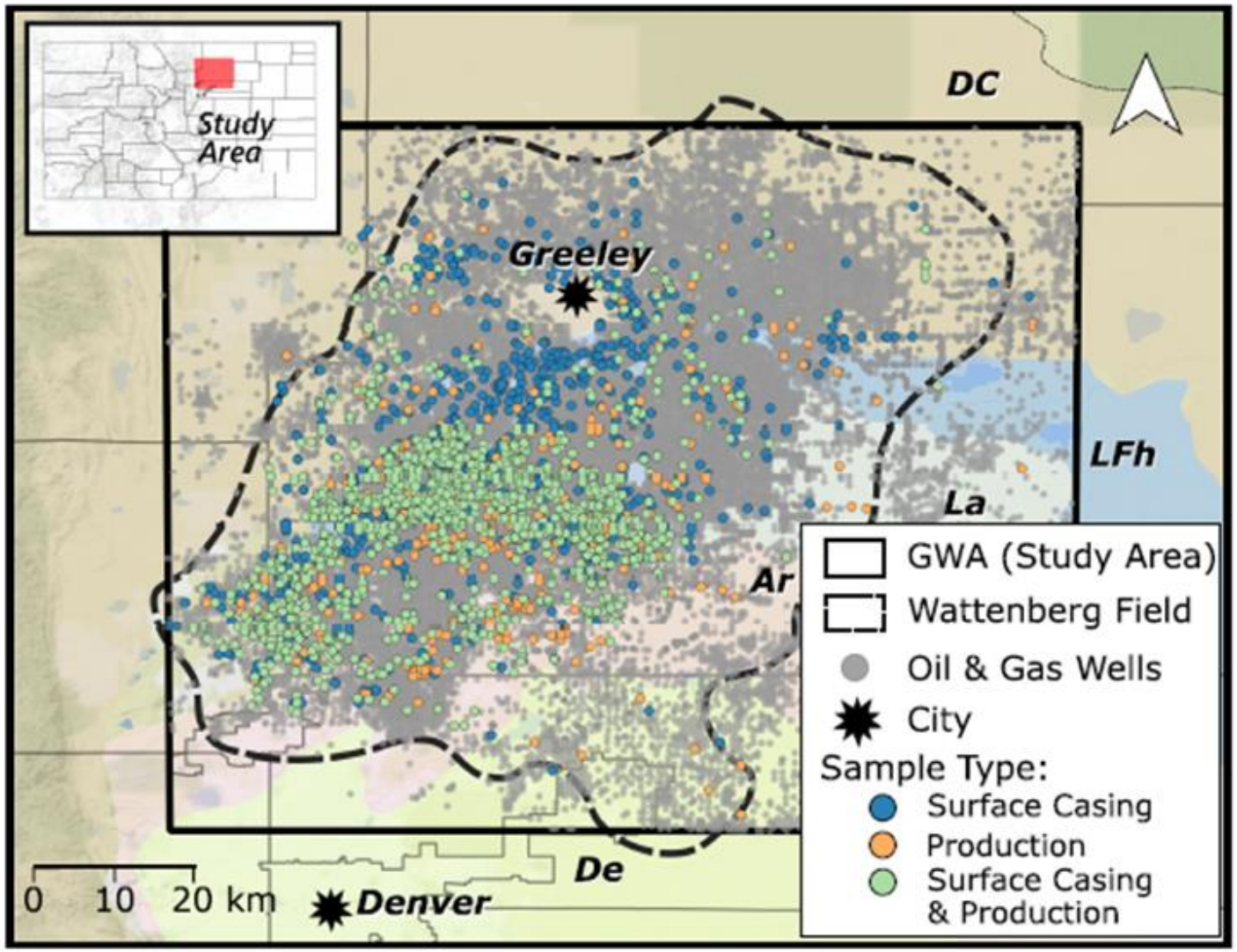
Illustration courtesy of Southwestern Energy

- Samples (gas, water, non-aqueous liquids) can be collected during bradenhead testing
- Composition and stable isotope analysis provide information about source of annular fluids and wellbore integrity

Bradenhead Sample Dataset

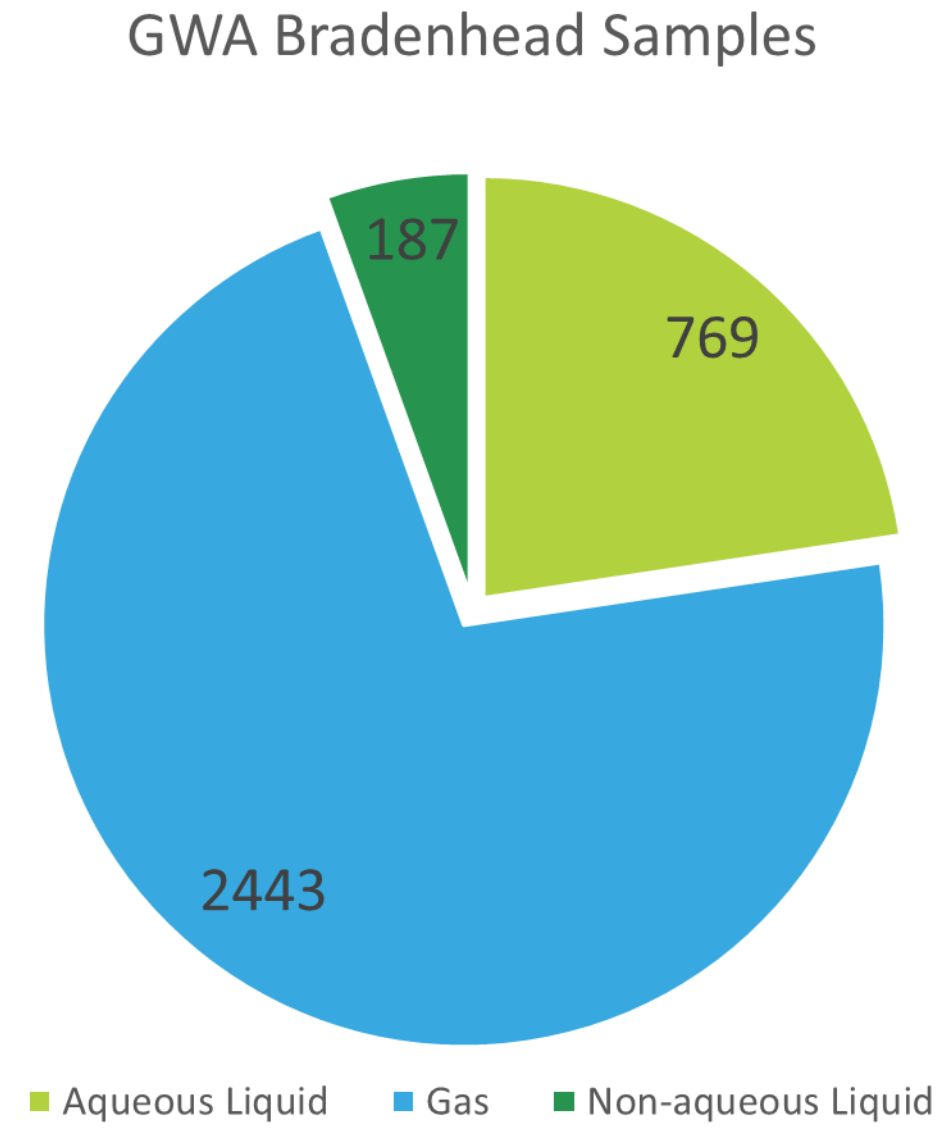


Example wellbore schematic with potential bradenhead migration scenarios (Lackey, 2022)



From Lackey et al, 2022

Bradenhead Sample Dataset



- Lackey et al. (2022) compiled data from n=3,399 samples in COGCC database
- Testing requirements differ for non-aqueous liquids, gases and waters
- Analytical data used to determine potential source of surface casing annular (bradenhead) pressure
- Most effective with paired samples from individual wells

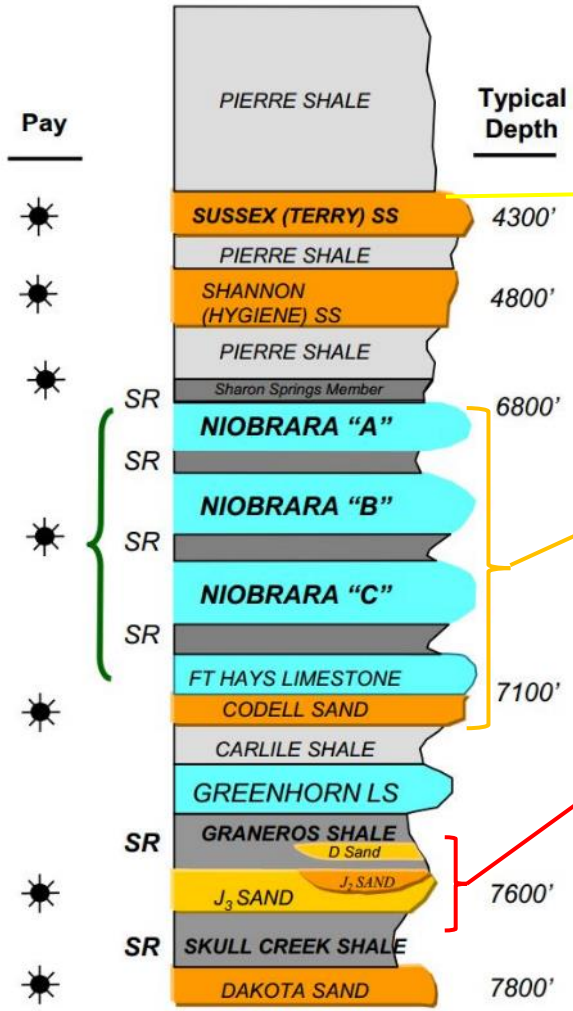
Bradenhead Gas Analysis

COGCC specifies:

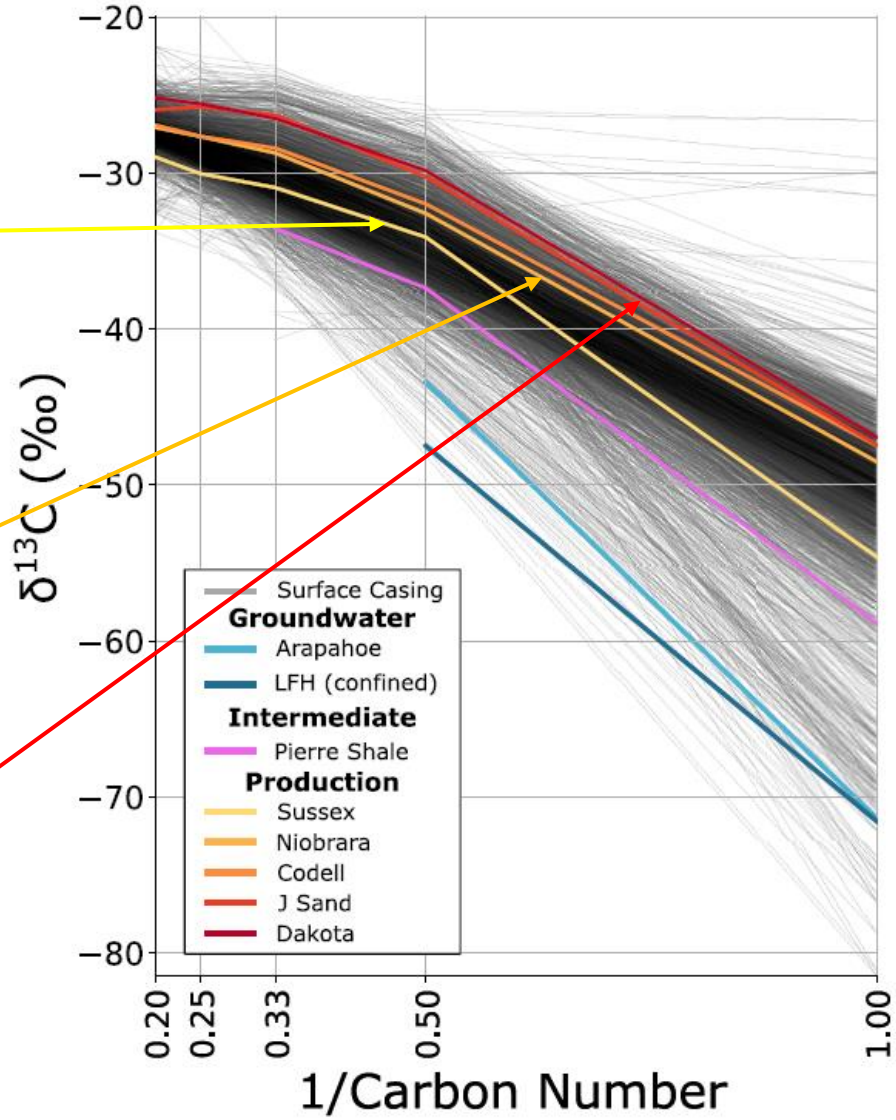
- Gas composition
- Stable carbon ($\delta^{13}C$, C_1–C_5 and CO_2) and hydrogen (δD C_1) isotope analysis

Applications:

- Biogenic/thermogenic
- Forensics

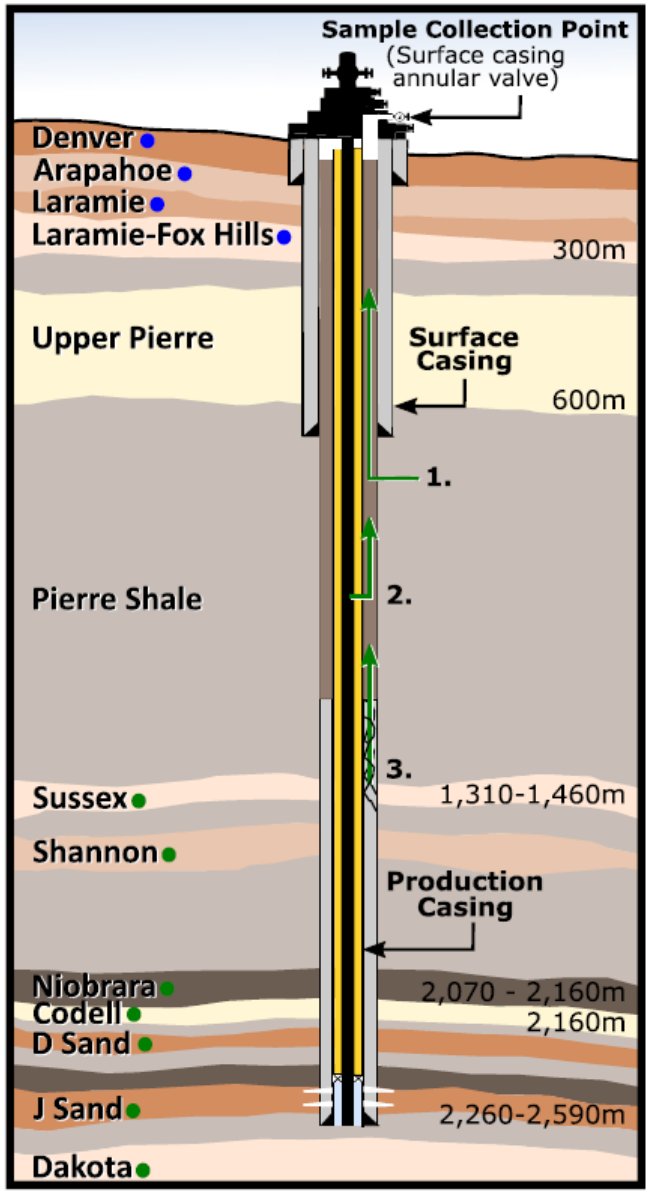


DJ Basin Stratigraphy (Sonnenberg, 2011)



Natural Gas Isotope Plot of Denver Basin surface casing and production gas samples (Lackey, 2022)

Bradenhead Gas Analysis



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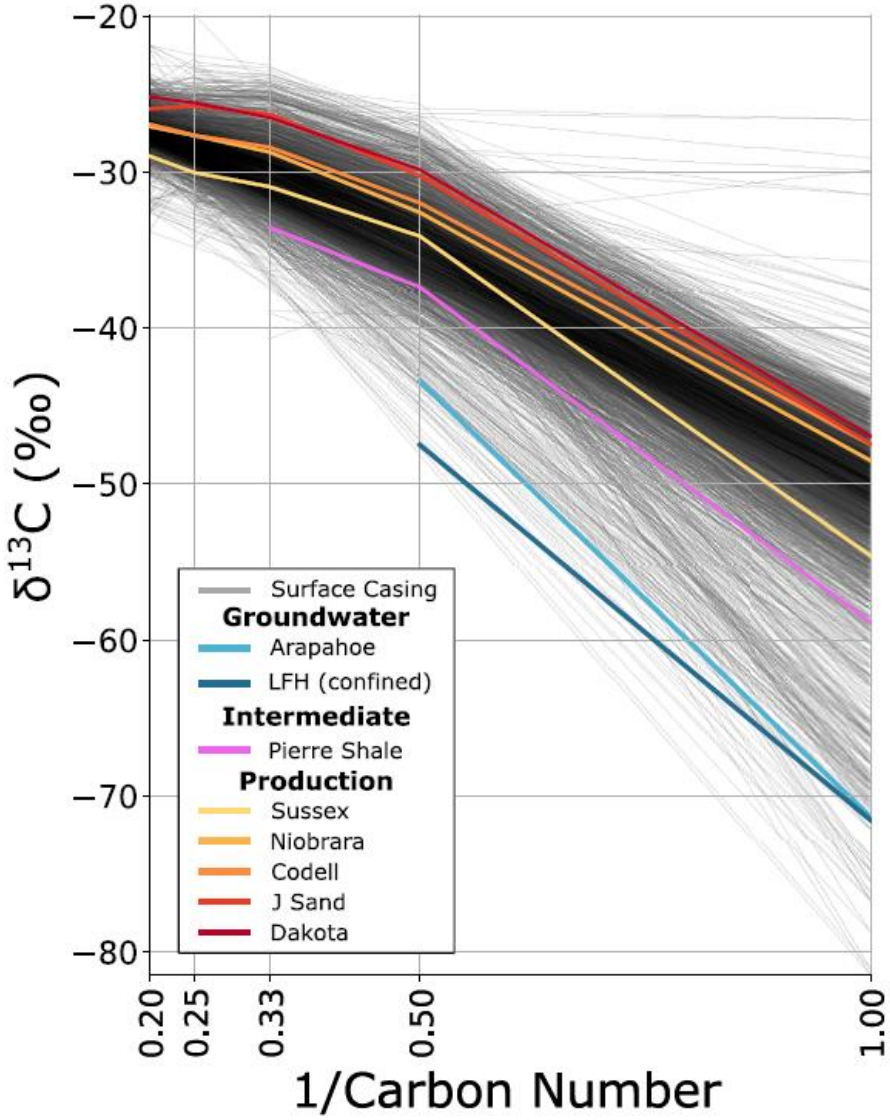


Natural Gas Isotope Plot of Denver Basin surface casing and production gas samples (Lackey, 2022)

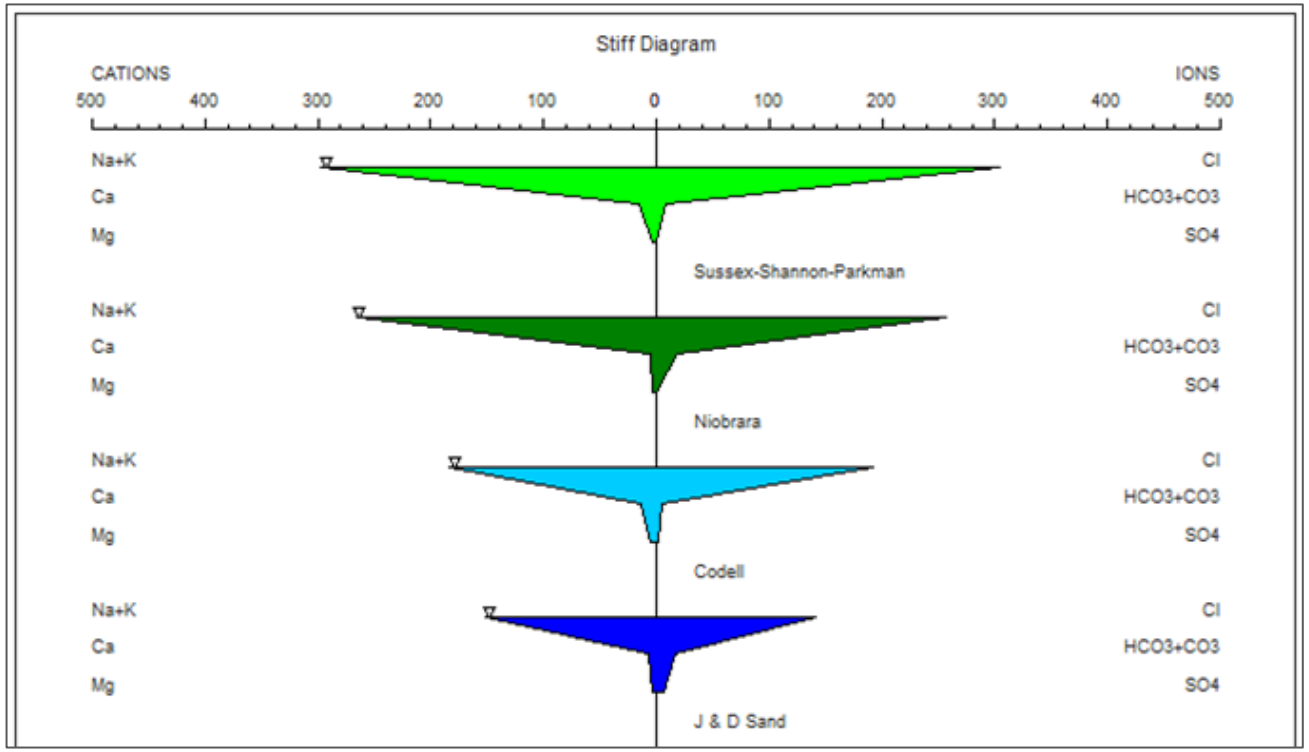
Bradenhead Aqueous Liquid Analysis

COGCC specifies:

- Major anions (Cl, CO_3, HCO_3, SO_4)
- Major cations (Na, K, Ca, Mg)
- TDS
- BTEX
- Dissolved Gases
- Diesel Range (DRO)
- Gasoline Range Organics (GRO)

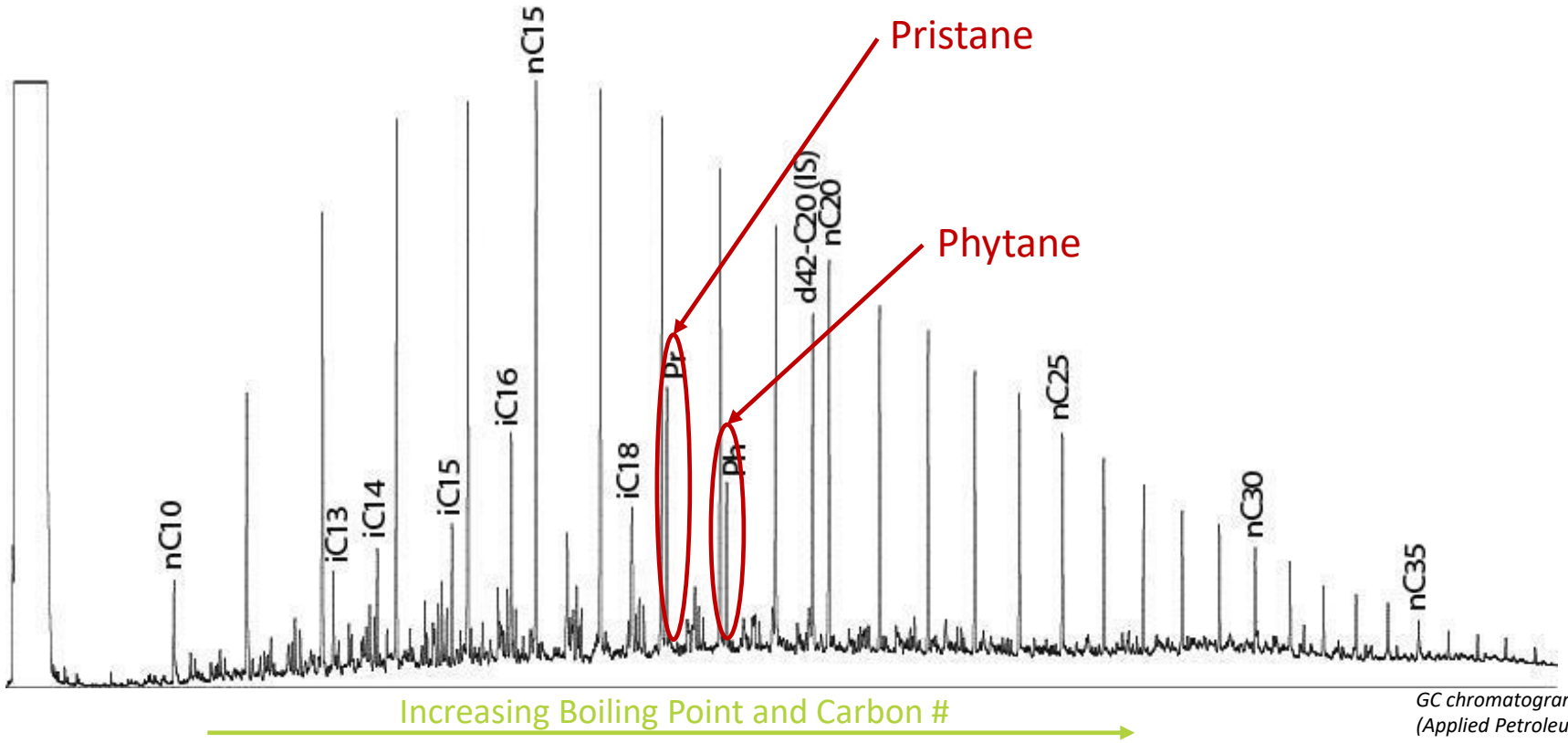
Applications:

- Forensics, though more limited
- Hydrocarbon content



Stiff Diagram of average produced waters from various formations in the Denver Basin (COGCC, 2022)

Bradenhead Non-Aqueous Liquid Analysis



GC chromatogram of crude oil courtesy of APT (Applied Petroleum Technology)

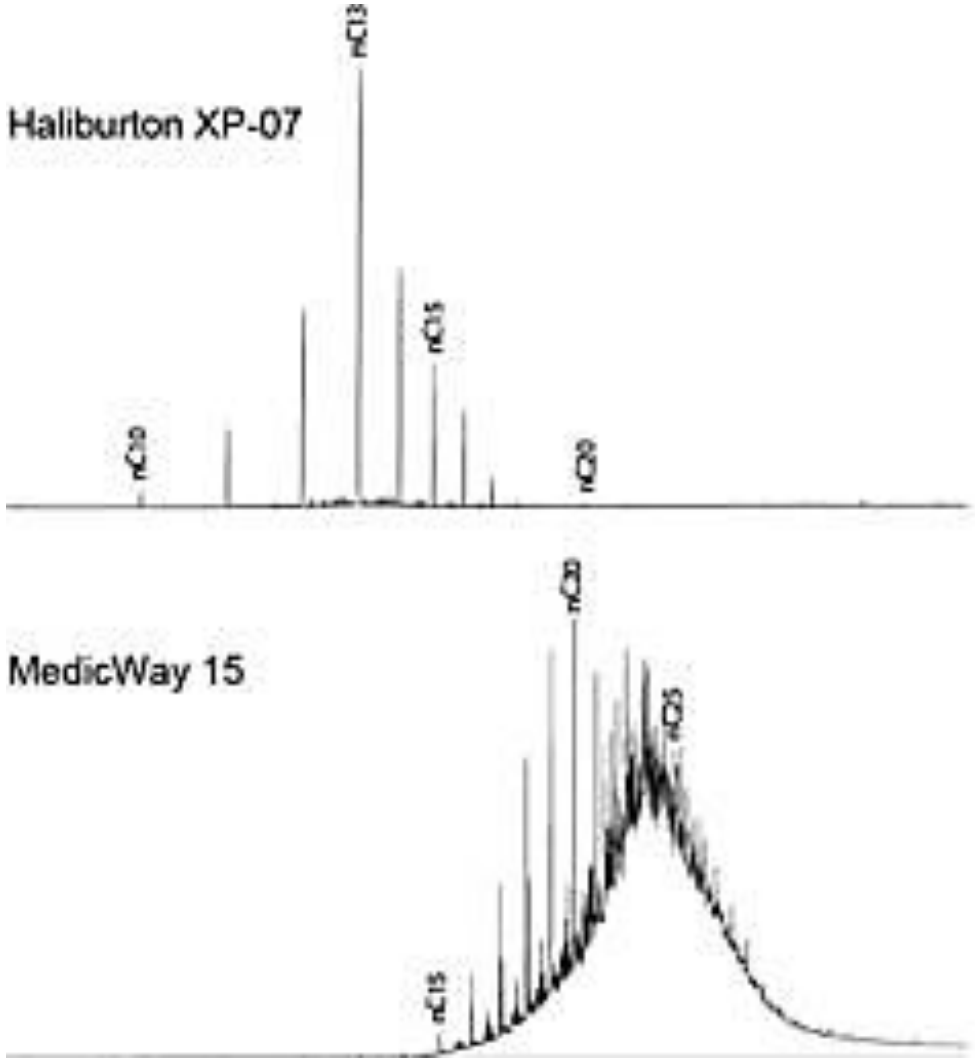
COGCC specifies:

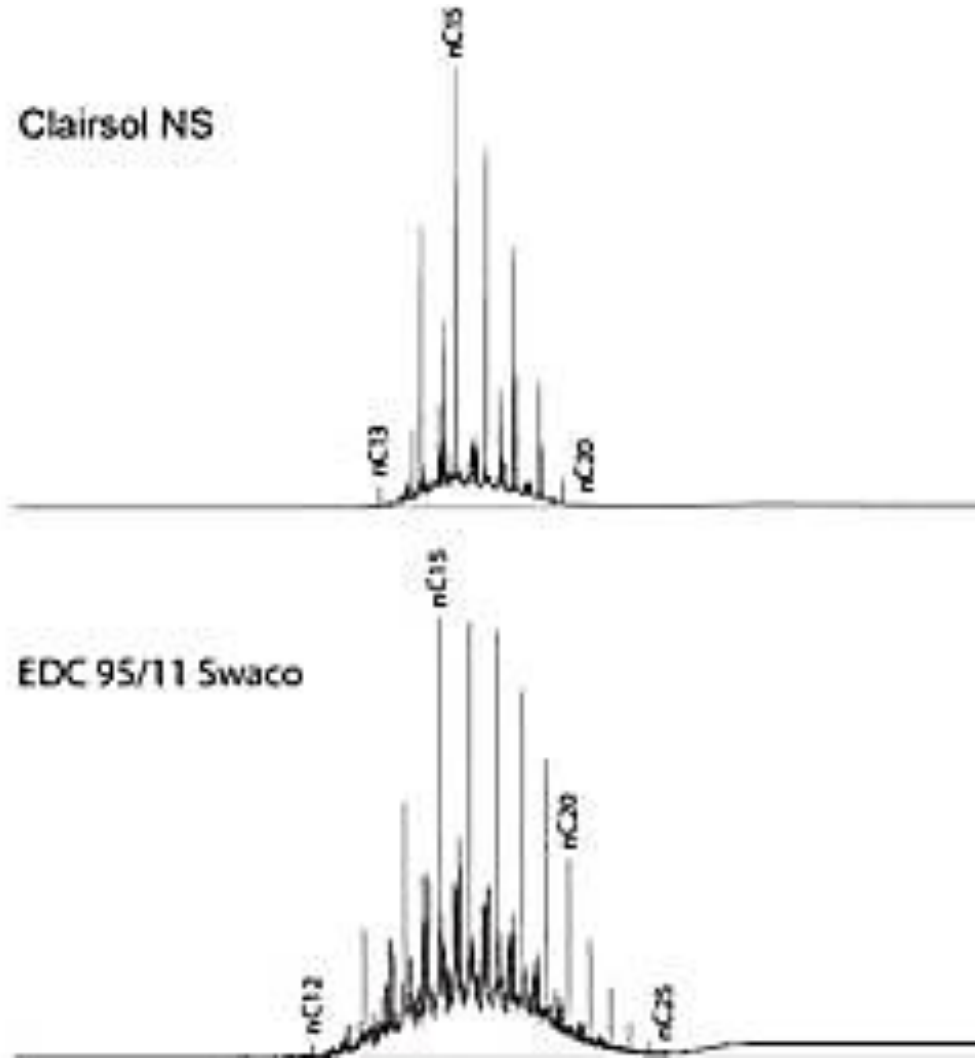
- Whole oil analysis, including
  - Pristane
  - Phytane

Applications

- Forensics (crude oil source formation)
- Degradation/ weathering
- Refined products vs crude oil

Bradenhead Non-Aqueous Liquid Analysis - OBMs





GC chromatograms courtesy of APT (Applied Petroleum Technology)

Summary

- Colorado's approach to sampling and analysis is unique
- Has resulted in > 60,000 samples
  - Groundwater monitoring
  - Bradenhead monitoring
- Useful for:
  - Setting baseline
  - Microbial (biogenic) vs thermogenic gas origin
  - Determining source of annular fluids and monitoring wellbore integrity
  - Forensic Investigations

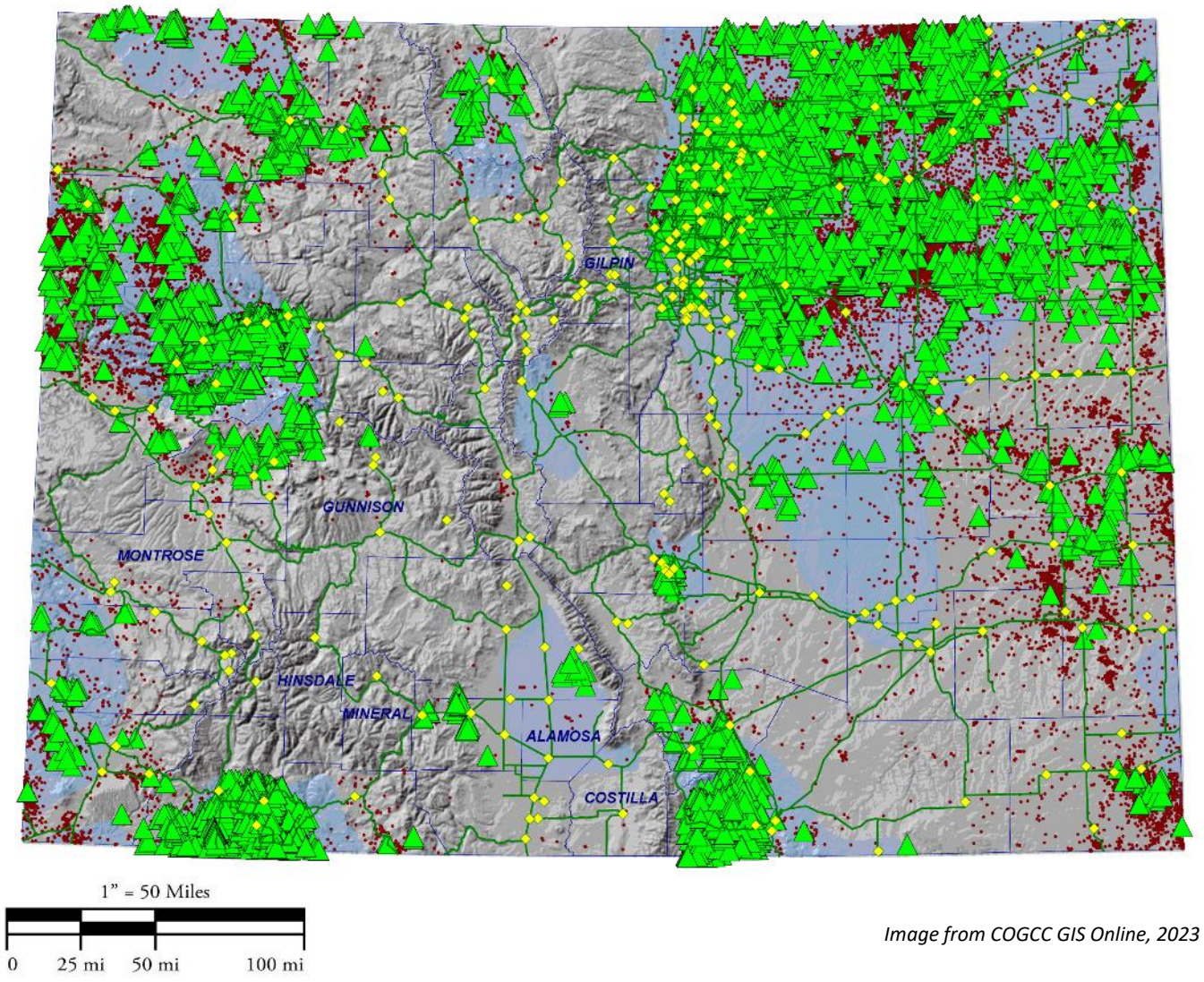


Image from COGCC GIS Online, 2023

Thank You!

Questions?

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