Summary

Geochemical Methods…
• Have been historically successful in reducing exploration risk, especially dry holes
• Geochemical methods are a general under-utilized tool
• Can be used on regional and prospect scales programs, onshore and offshore
• Can be used to compare reservoir to seep composition
• Are best utilized combined with multiple methods to reduce risk and false positives
• Should be implemented with adequate sample size and spacing
• Will expand in capabilities due to technology improvements and sensitivity

What will change?
• continued improvements in technology & sensitivity
• Ability to measure stable isotopes at low concentrations
• Ability to process more data & variables
• Improved remote sensing technologies
• Better understanding of seep and migration mechanisms

Selected References


Past, Present and Future Advancements in Methods for Detecting Hydrocarbon Seepage after 75 Years

John V. Fontana¹, PG and David M. Seneshen¹, PhD

Session Title: History of Petroleum Geology Forum (AAPG)
Sunday, May 19, 2013
Session Chairs: Stephen Testa, Larry Woodfork
Outline

- **PAST**
  - Macroseep vs. Microseep
  - First Known Methods – Russia & Germany
  - The American Pioneers
  - Methods & the Sensitivity Issue

- **PRESENT**
  - Landmark Symposia & Publications
  - The Theory of Vertical Migration
  - Direct Detection vs. Indirect Detection Methods of Seepage
  - Methods of Sampling & Analysis
  - Modern Methods of Seep Detection
  - Analysis of an Anomaly

- **FUTURE**
The Past

“Practical Oil Geology”

  - Foreword: Oil Geology – Applied Common Sense:
    - “There is at present a rather vague idea in the minds of many men as to just what constitutes an oil geologist. Some people associate him with the ‘crooked stick’ or ‘peach tree twig’ men, others think he used hocus-pocus, and as yet, comparatively few of the operators see the geologist as a clean-cut, clear-thinking engineer who is just as much an expert in his line as is the driller or railroad surveyor.”
  - Geochemistry – Yet to be discovered as a tool?!
Was Jed Clampett the original exploration geochemist?

Drilling next to a visible oil seep (a macroseep) was the earliest method used to find oil traps.

Today – Near-surface exploration geochemistry methods use sensitive instrumentation to detect invisible microseeps.
Macroseep vs. Microseep

**Macroseeps**
- Jed Clampett Style
- Strong Gas/Petroleum Flux
- Visible Expressions or.....
- Measured in Field or by Remote Sensing Methods

**Microseeps**
- Direct Detection Methods
  - Sensitive Laboratory or Field Methods
- Indirect Detection Methods
  - Alterations Due to Bacterial & Red-Ox Changes
  - Gases or Elements Related to the Reservoir
  - Remote Sensing for Alteration
Mud (and Methane) Volcanoes of Azerbaijan
Macroseeps Seen from Space

NASA satellite photograph showing oil slicks from natural seeps in the Gulf of Mexico, offshore Louisiana. (NASA)
Less Obvious Macroseeps
The First

- **First Geochemical Survey Done in Germany, 1929, Published by G. Laubmeyer in 1933**
  - Measured methane using microcalorimeter.

- **Russian paper in the same year.**
  - Sokolov was able to measure methane and ethane.
Ludwig W. Blau of Humble Oil & Refining Co. (now ExxonMobil)
- Contended many geophysical highs were velocity anomalies from alteration and was opposed to using reflection seismography.

Eugene Rosaire & Eugene McDermott noted unique mineralization above Texas fields.
- Both Geophysicists and pioneers in seismography were so convinced they started a geochemical service company.

Leo Horvitz developed innovative hydrocarbon detection methods
- Developed an acid extraction method to measure adsorbed (or occluded) gases and concentrate the gases to enable analysis of $C_1$-$C_4$ hydrocarbons.
Mainly Direct Detection of Hydrocarbons

Methane, Ethane, & Other Gases as Technology/Methods Improve
- Instrument Sensitivity was Limiting

Visible Alterations from Gas Seepage
- Reducing & pH Conditions
The Sensitivity Issue

- Extracting and concentrating gases increased sensitivity.

From Leo Horvitz, 1969
Repeated Surveys Yielded Evidence Seeps are Live

- Surveys in Texas field 22 years apart, 34 years after production started & 375,000 bbls produced.

From Leo Horvitz, 1969
Landmark Symposiums and Publications

- **Unconventional Methods in Exploration for Petroleum & Natural Gas**
  - Four Meetings Held, 1968 – 1985
  - Institute for the Study of Earth & Man at Southern Methodist University
  - Four Proceeding Volumes Published
  - Eds. Heroy, Gottlieb, Davidson

- **1984, AAPG - Joint NASA/Geosat Test Case Project,**
  - Jet Propulsion Laboratory, California Institute of Technology
  - Ed. Michael Abrams
Landmark Symposia

- Bibliography for Near Surface Prospecting Methods
  - APGE Special Publication No. 2
  - 1988, Peter K. H. Groth,
- Soil Gas & Related Methods for Natural Resource Exploration
  - 1993, Ronald Klusman (Colorado School of Mines)
- Surface Exploration Case Histories; Applications of Geochemistry, Magnetics and Remote Sensing
  - AAPG Studies in Geology No. 48 and SEG Geophysical Reference Series No. 11:
    - 2002, Editors D. Schumacher and L. LeSchack
Landmark Symposia and Publications

- **AAPG Hedberg Research Conferences**
  - 1994, Hydrocarbon Microseepage and Its Near-Surface Expression
  - 2002, Near-Surface Hydrocarbon Migration: Mechanisms and Seepage Rates
  - 1996 Publication: AAPG Memoir 66; Hydrocarbon Migration and Its Near-Surface Expression. (from the 1994 conf.)
  - Editors D. Schumacher, M. Abrams
Theory of Vertical Migration & Microseepage

- Diffusive - Effusive – Gravity – Buoyancy?
- Effusion is responsible for the “Escape.”
- Gravity and Buoyancy best explain the near-vertical migration to the surface.
- Diffusion does not explain the patterns we see but is more likely a part of the equation above the water table (vadose zone.)
Modified after Saunders et al. 1999

\[
\text{Fe}_2\text{O}_3 + 2\text{H}_2\text{S} = \text{FeS}_2 + \text{FeO} + 2\text{H}_2\text{O}
\]

\[
2\text{HCO}_3^- + \text{Ca}^{2+} = \text{H}_2\text{O} + \text{CO}_2 + \text{CaCO}_3
\]

\[
\text{H}_2\text{S} \leftrightarrow 2\text{H}^+ + \text{S}^{2-}
\]

\[
4\text{UO}_2^{+2} + \text{S}^{2-} \rightarrow 4\text{UO}_2^{+} + \text{S}^{6+}
\]

\[
\text{H}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}
\]

\[
\text{H}^+ + \text{SO}_4^{2-} + \text{CH}_4 \rightarrow \text{CO}_3^{2+} + \text{H}_2\text{S}^+ + 2\text{H}_2\text{O}
\]
Evidence of Alteration
Bleaching of Red Sandstone, East Texas Basin

A camouflaged rig on Island Grissom, a man-made drilling island near Long Beach, CA. *Photo by J. Jepson.*
Documented Macroseeps


  - >10,000 Macroseeps Documented Worldwide

- Etiope, Giuseppe, 2009, GLOGOS, A New Global Onshore Gas-Oil Seeps Dataset

- If we have documented this many visible macroseeps, how many microseeps are there?
Direct Methods
- Detects actual migrated hydrocarbon species that have seeped from the reservoir and accumulated in the near-surface.
- Today, Comparing Reservoir Fluid and Gas Composition to Seep Composition is Possible

Indirect Methods
- Detects visible, chemical and biological alterations from migrating hydrocarbons caused by altering redox conditions, mineralization, microbial activity, etc.
Direct vs. Indirect

**Direct Methods**
- Ambient Air Seeps
  - Infra-Red Spectrometers
  - Portable Gas Detectors
- Soil Gas Hydrocarbons
  - Interstitial, Occluded or Adsorbed Gases
  - Passive Soil Gas Collection
- Liquid Hydrocarbons
  - Solvent Extracted Oils
  - Scanning Fluorescence
  - Extended GC or GC-MS
  - Satellite or Fluorescence Imaging
- Offshore
  - Subsurface “Sniffers”

**Indirect Methods**
- Remote Sensing
- Geomorphology
- Mineral Alterations
- Trace Metals
- Radon, Radiometrics
- Iodine
- Microbial
- Helium
- Botanical Stress
- Geophysical Methods
  - Magnetics
  - Velocity Changes
  - Sonar Images (offshore)
Finding the Less Obvious

- Ambient Air IR Survey
  - Truck, ATV, Boat or Helicopter-Mounted
  - Rapid data collection system
  - Detects gas seep “plumes”
  - Locates infrastructure leaks.

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Ambient Air IR Survey Real Time Results

- CH₄, CO₂ and Heavier (C₂+) Hydrocarbons
- <1 ppm Sensitivity for Methane
- Continuous GPS/GIS Enabled Acquisition
- Wind (Gas Plume) Direction Recorded
Ambient IR Road Survey
Intensity & Wind Direction

Legend
Old_Well_Sites
Status
- D&A
- D&A-G
- D&A-OG
- GAS
- Proposed Well Pads

IR_LDS_Tracks_110507
IR_LDS_Methane_PPM
METHANE_PPM
- 0.4 - 1.0
- 1.1 - 5.0
- 5.1 - 10.0
- 10.1 - 20.0
- 20.1 - 100.0
- 100.1 - 373.2
Portable FID/PID on Foot Surveys Locate Gas Seeps

- **Flame Ionization (FID)**
  - Detects Hydrocarbon Gases
  - 1ppm CH₄ Sensitivity
- **Photo Ionization (PID)**
  - Heavies & Aromatics
  - 0.1ppm Sensitivity
- Continuous Surface measurements
- Calibrated Detectors
Improvements in Sensitivity

- Gas Chromatography
  - PPB or PPT Sensitivity
- Stable Isotope Analysis
- Satellite & Remote Sensing
- Portability
Trace Analysis Methods

- **Gas Range (Light) C₁-C₆ Hydrocarbons**
  - Parts Per Billion (ppb) Levels
  - Free Gas or Head-Space Gas
  - Thermally Desorbed (low & high temp)
  - Acid Extracted
  - Adsorbents (Passive Soil Gas) ng or ppt

- **Liquid Range (C₆+) Hydrocarbons**
  - PPB and Parts Per Million (ppm) Levels
  - Solvent Extracted
    - Spectral Fluorescence
    - High Resolution GC-FID
  - Thermally Desorbed
    - High Resolution GC/FID or GC/MS
    - Adsorbents (Passive Soil Gas)

- **Trace Metals**
  - Acid Extracted Soils - ICP/MS
Sampling Media Available for Geochemical Analysis

- **Shallow Soils**
- **Shot-hole Sediments**
- **Lake Sediments**
- **Vegetation**
- **Deep Soils**
- **Ground or Sea Water**
- **Free Soil Gas**

![Diagram with labels: Adsorbed, Occluded, Interstitial or Dissolved]
Passive Soil Gas Methods

- Invented at Colorado School of Mines,
  - Klusman & Voorhees, 1980’s
- Also called “Integrative” Soil Gas
- Activated Adsorbents Buried in Soil/Sediments
- Concentrates Gases and Smooths Variations
- Detects C$_2$ – C$_{20}$ Hydrocarbons
- Thermal Desorption GC and GC/MS
- Independent of the Matrix
SYNCHRONOUS SCANNED UV-FLUORESCENCE

**Spectra of Three Oils with Different Gravities**
- High Gravity Cretaceous Condensate
- Medium Gravity Cretaceous Oil, Colorado
- Low Gravity Paleozoic Oil, Nevada

**Aromatic Hydrocarbon Groupings**
- 1 Ring
- 2 Ring
- 3-4 Ring
- 5+ Ring

0
200
400
600
800
1000

Fluorescence Intensity (millivolts)

250 300 350 400 450 500

Emission Wavelength (nanometers)

300 400 500 600

Wavelength (nm)

0
2
4
6
8
10
12

Intensity (a.u.)
Historically, a Detection WAS an Anomaly!

Lower Sensitivities Mean We Can Now Detect Background Everywhere

Isotopes (d$^{13}$C, dD) of Larger Seeps

To Distinguish Background from Anomaly:

- Fingerprinting Reservoir Gases and Fluids
- Adequate Sample Density
- Multivariate Statistical Analysis
- Integration with Other Methods
Liquid Hydrocarbon Seep Anomalies
Albion-Scipio Oil Field
(Prospect Level Sample Spacing)

Before Drilling

After Drilling

Fluorescence spectral pattern for oil seep.
Fluorescence spectral pattern of reservoir oil

0 500 Meters

0 500 Meters
Jonah & Pinedale Tight Gas
Light Hydrocarbon Gases
Regional Scale Sampling
Trace Metals in Sagebrush
Cadmium, Nickel, Barium Factor
Covenant Field
Light Hydrocarbons

- Utah Overthrust
- HTTD Method
- Wet Gas Ratio in Desorbed Soil Gas
  - % nC₄/C₁
- Apical- & Fault-Related Anomalies

Geology Legend
- Quaternary Alluvium and Colluvium
- Quaternary Landslide Deposits
- Oligocene Volcanics
- Miocene Volcanics
- Jurassic Summerville, Entrada, Carmel, Arapien, Twin Creek Fms

Percent nButane (%nC₄/C₁+)
- 0.20 - 3.14
- 3.15 - 3.68
- 3.69 - 4.30

Kilometers

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Covenant Field Fluorescence

- Synchronous Scanned Fluorescence (SSF)
- Trace Light Oils (Spectral Similarity)
- Apical & Fault Anomalies
Success of Geochemical Exploration Methods

Robert Potter II, et. al. (1994) Santa Fe Minerals Inc. Chapter 33 in AAPG Memoir 66
The Future?
What Will Change?

- Continued Improvements in Technology & Sensitivity
- Ability to Measure Stable Isotopes at Low Concentrations
- Ability to Process More Data & Variables
- Improved Remote Sensing Technologies
- Better Understanding of Seep and Migration Mechanisms
Geochemical Methods...

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- Geochemical Methods are a General Underutilized Tool
- Can be Used on Regional and Prospect Scales Programs, Onshore and Offshore
- Can be Used to Compare Reservoir to Seep Composition
- Are Best Utilized Combined with Multiple Methods to Reduce Risk and False Positives
- Should be Implemented with Adequate Sample Size and Spacing
- Will Expand in Capabilities Due to Technology Improvements and Sensitivity
QUESTIONS?

PLEASE DRIVE & DRILL RESPONSIBLY!

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