Hydraulic Fracturing Fluid Forensics: Potential and Pitfalls

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Overview

• What makes a good forensic marker?
  ▪ Detection
  ▪ Attribution

• What chemical signatures have been used previously?
  ▪ Total dissolved solids, major ions
  ▪ Naturally occurring radioactive material (NORM)
  ▪ Petroleum hydrocarbons
  ▪ Methane isotopes

• Potential new markers
  ▪ Specific chemicals
  ▪ Isotopic signatures

• Which have potential? Which have pitfalls?
What makes a good forensic marker?

**Detection**
Is the signal big enough to (cost effectively) measure?

**Attribution**
Is the signal unique enough to point to a specific source?
Detection vs. Attribution
Where can we look for forensic markers?

- Fracturing fluids
- Flowback water
- Produced water
- Groundwater/drinking water
- Surface water (e.g., lakes, streams)
Fracking Fluids, Flowback, and Produced Water

- Fracking fluids injected under pressure
- “Flowback” returns to the surface
- Produced water common to all oil and gas extraction

USGS, 2011
Chemical Signatures of Hydraulic Fracturing

- Total dissolved solids and major ions
- Naturally occurring radioactive material (NORM)
- Petroleum hydrocarbons, BTEX
- Methane isotopes (C, H)
Total Dissolved Solids and Major Ions

USGS, 2012
Total Dissolved Solids and Major Ions

USGS, 2012
Total Dissolved Solids and Major Ions

- Easy to detect
  - High concentration
  - Routine measurement
- Difficult to attribute
  - Alternative sources (e.g., road salt)
  - May attribute to formation
  - Common to all produced water
  - Signature changes during transport (precipitation, dissolution of salts)
  - Produced water recycling could complicate interpretation
NORM (e.g., radium, uranium isotopes)
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EXPLANATION
- Red: Total radium
- Blue: Ra-228/Ra-226

Day 0-20: Days since initiation of flowback
0-7000: Total radium in picocuries per liter
0.10-0.40: Ra-228/Ra-226 in picocuries per liter

USGS, 2011
NORM (e.g., radium, uranium isotopes)

- Not easy to detect in water
  - May be easier in sediments: Warner *et al.* (2013) study at Josephine brine facility
- Attribution not very specific
  - May attribute to a formation
  - Common to all produced water
Petroleum Hydrocarbons

Phase 3

Phase 4

US EPA, 2011
Petroleum Hydrocarbons

Crude Oil

Diesel Oil

US EPA, 1992
Petroleum Hydrocarbons

• Possibly easy to detect
  ▪ Hydrocarbon fingerprinting is routine with standard methods
  ▪ Depends on dilution

• Moderately easy to attribute
  ▪ Bulk methods like TPH (GRO, DRO) are NOT specific enough
  ▪ Highly specific components (biomarkers) difficult to detect
  ▪ Volatile compounds (BTEX) evaporate
  ▪ Biodegradation may affect signature
  ▪ Many potential sources
Methane Isotopes

US EPA, 2011
Methane Isotopes: Case Studies

- **Osborn et al., 2011**
  - Groundwater near Marcellus Shale
  - Isotopes show thermogenic signature

- **Molofsky et al., 2013**
  - Groundwater near Dimock, PA
  - Isotopes show thermogenic signature
  - Could not distinguish between Marcellus gas and shallower gas in casing string annular spaces

- **Warner et al., 2013**
  - Groundwater near Fayetteville Shale
  - Concentration not higher near production wells
  - Isotopes do NOT show thermogenic signature
Methane Isotopes

• Hard to detect
  ▪ Need enough methane to get a robust isotopic measurement

• Attribution not very specific
  ▪ Biogenic vs. thermogenic
  ▪ Most samples are somewhere in the middle
  ▪ Thermogenic gas not specific to hydraulic fracturing
Potential New Markers

• Isotope analysis of brines, gases
• Compound specific isotope analysis
• Specific chemicals in fracking fluids
• Tracers (e.g., perfluorinated compounds) intentionally added to fracking fluids
Detection vs. Attribution
Detection vs. Attribution

Salts, major ions
Water isotopes
Methane isotopes
NORM

Petroleum hydrocarbons
Compound-specific isotopes
Added tracers
Detection vs. Attribution

- Salts, major ions
- Water isotopes
- Methane isotopes
- NORM

- Petroleum hydrocarbons
- Compound-specific isotopes
- Added tracers
Questions?
NORM (e.g., radium, uranium isotopes)

\[ \text{Log total Ra} = 1.55 \times \text{Log TDS} - 4.86 \]
Water Isotopes

Advanced Resources International, Inc., 2005
Oxygen and Hydrogen Isotopes

• Reasonably easy to detect
• More difficult to attribute
  ▪ Distinct isotopic signature of formation water
  ▪ Mixing between shallow groundwater and deep source may look like a different source
Methane Concentrations

US EPA, 2011