Considerations for Determining the Source of Groundwater Contamination Associated with Hydraulic Fracturing

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Possible Causes and Baseline Sampling

- Possible causes
  - Well construction failure
  - Migration of hydraulic fracturing (HF) fluids/gases to aquifers via fractures
  - Surface spills
- Baseline sampling
  - Major cations/anions (charge balance)
  - Metals/non-metals
  - Dissolved gases and isotopic signatures
  - HF fluid (recycled water?) and produced water chemistry
  - pH, ORP, SC, DO, temperature (USGS low pump)

Diagram: Scott Detrow and Yan Lu/StateImpact Pennsylvania

Ability to Detect Presence in Groundwater

- Geologic issues
  - Characterization of fractures and degree of interconnectedness (before/after HF)
  - “Proper” placement of monitoring wells
  - Distance between HF zone and DW aquifer
- Chemical issues
  - Reliability of analytical methods
  - Detection limit vs concentration in situ
  - Thermal/biological degradation of HF chemicals

Inconclusive Indicators

- Constituents in formation water alone
  - TDS, sulfate, methane
- Compounds are naturally occurring
- Can’t prove source is hydrofracking chemicals from formation
- Problem distinguishing methane released from HF vs methane slowly migrating from formation

Better Possible Indicators

- Anthropogenic HF chemicals and produced water constituents
  - Benzene, alkylated aromatics, PAHs occur in both
  - Focus on HF compounds with highest concentrations
  - Alcohols, including glycols and glycol ethers, dioxane, acrolein, and bis-(2-chloroethyl) ether
  - Acrylonitrile
    - Detected in water and air above flowback storage ponds
    - Haliburton patent for polymerization process for formation of acrylonitrile-butadience-styrene polymer on surface of proppants
  - Utilization of anthropogenic indicators is difficult in the absence of reporting of the chemicals used in HF

Aquifer Water Quality Degradation from Stimulation of SRB Activity

- Hypothesis: Sulfate-reducing bacteria (SRB) activity promoted by increased presence of natural gas components (> 30 mg/L methane) from HF activity
- Dimock PA: Substantial reduction in drinking water quality
- Elevated sulfide (up to 6 mg/L) and pH (up to 9.8)
- Lower redox state of water promotes increased reduction/dissolution of Fe, Mn, and, increased pH increases Al
- Use of the well for drinking water discontinued several months after HF

Boron / Boron Isotopes

- Used in HF solutions – crosslinker, pH control on solubility
- ~70 HF products contain boron
- Boron isotopes δ11B ($^{11}B/^{10}B$)
  - Naturally occurring in produced water/formations
  - Used in Israel to distinguish sewage-affected water from pristine groundwater
  - Used to distinguish B sources in oilfield brines (Carty et al., 1999)
- *Advantages*: B doesn't degrade thermally or biologically; conservative and mobile; detection limit not issue
  - Total B: ICP-MS - MRL = 0.5 μg/L; MDL = 0.2 μg/L
  - B isotope method highly sensitive
- *Challenges*: need high enough concentrations and different isotopic signatures in HF fluid and produced water

Summary

- Geologic and thermo/bio/chemical constraints
  - Need advances in ability to “see” in subsurface
- Detection of anthropogenic HF chemicals more telling but more challenging than detection of produced water constituents
- Boron isotopes: underused but promising approach
- Increased SRB activity due to increased natural gas metabolism may be responsible for reduction in drinking water quality. Baseline data should examine SRB indicators
- Highlights importance of defining adequate baseline sampling and monitoring network, in addition to identifying promising indicators
- Sensitive and specific methods are critically important