Hydraulic Fracturing Fluid Forensics: Potential and Pitfalls

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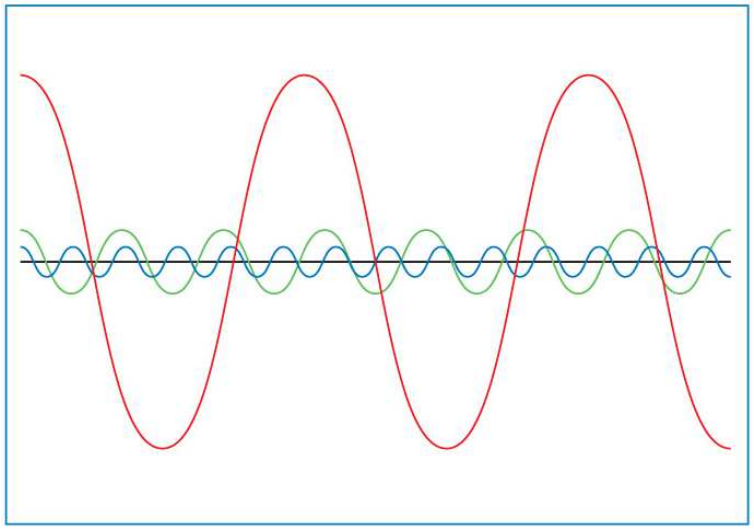
Overview

- 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?

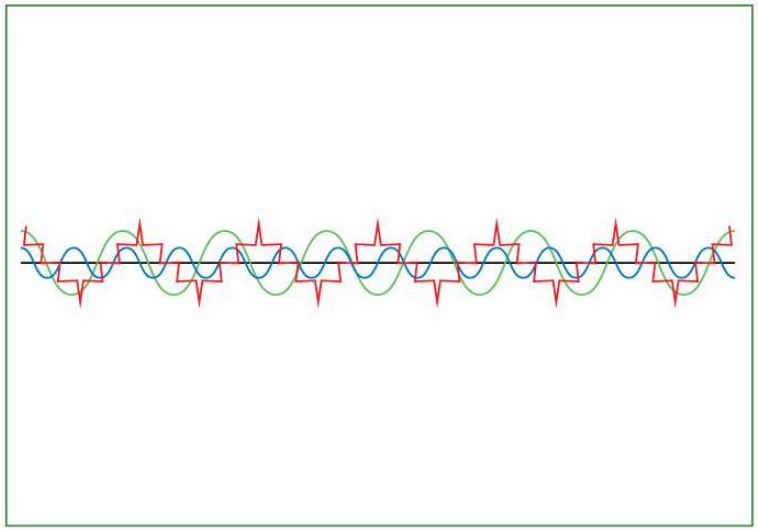
Detection

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



Attribution

Is the signal unique enough to point to a specific source?



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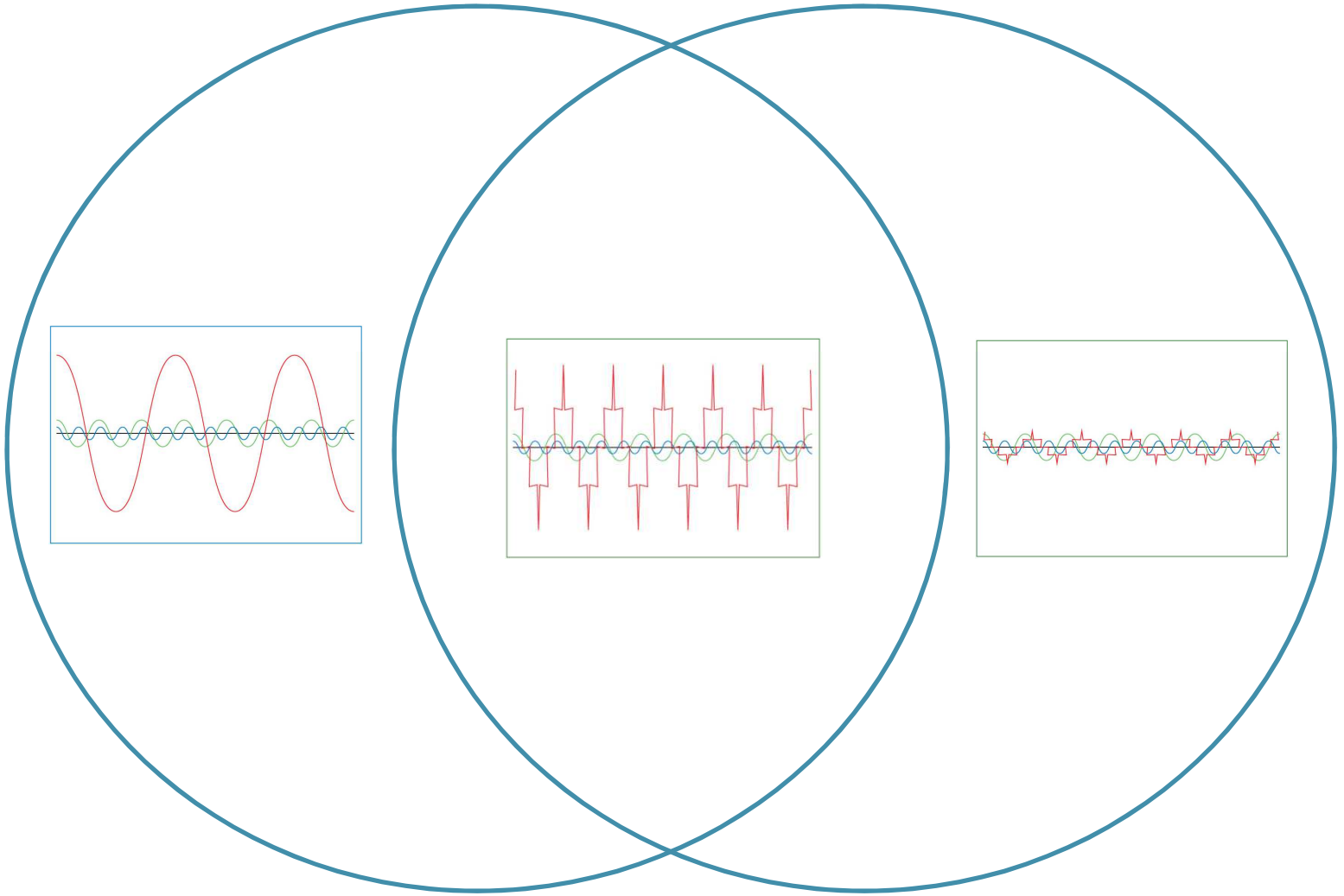
Detection *vs.* Attribution



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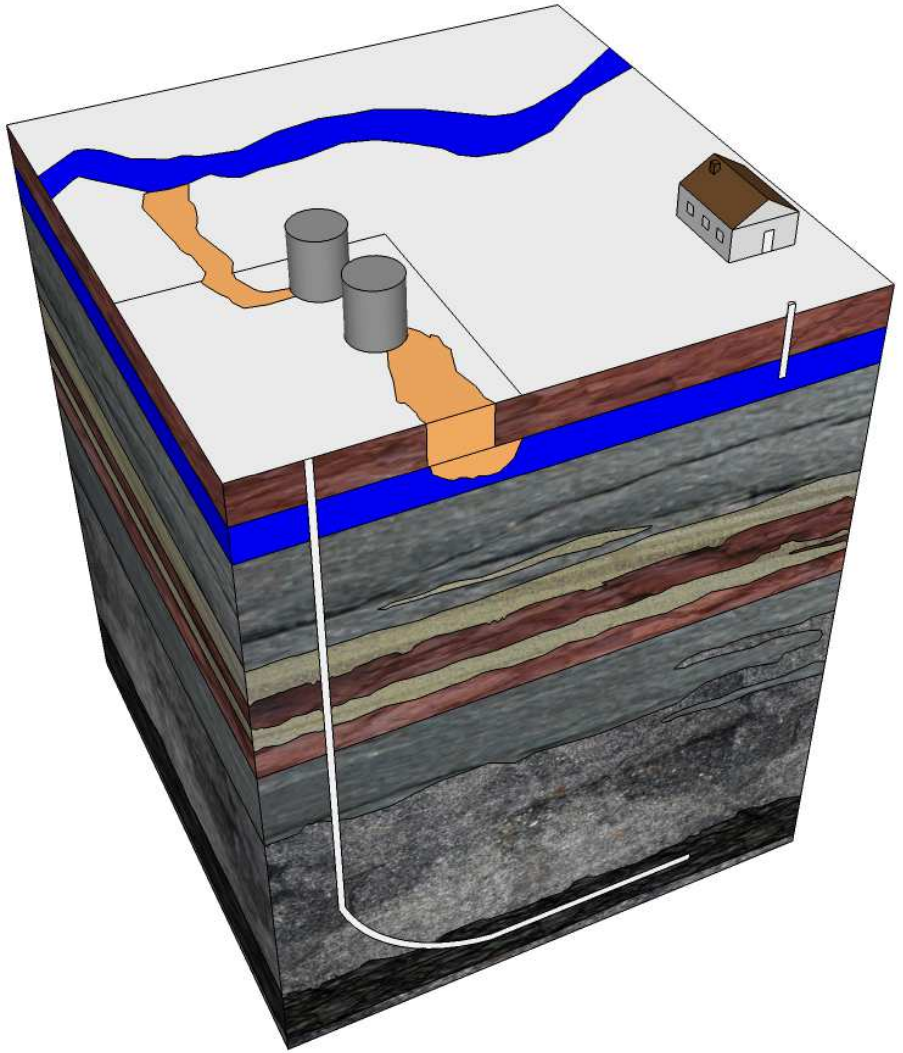
Where can we look for forensic markers?

- Fracturing fluids
- Flowback water
- Produced water
- Groundwater/ drinking water
- Surface water (*e.g.*, lakes, streams)



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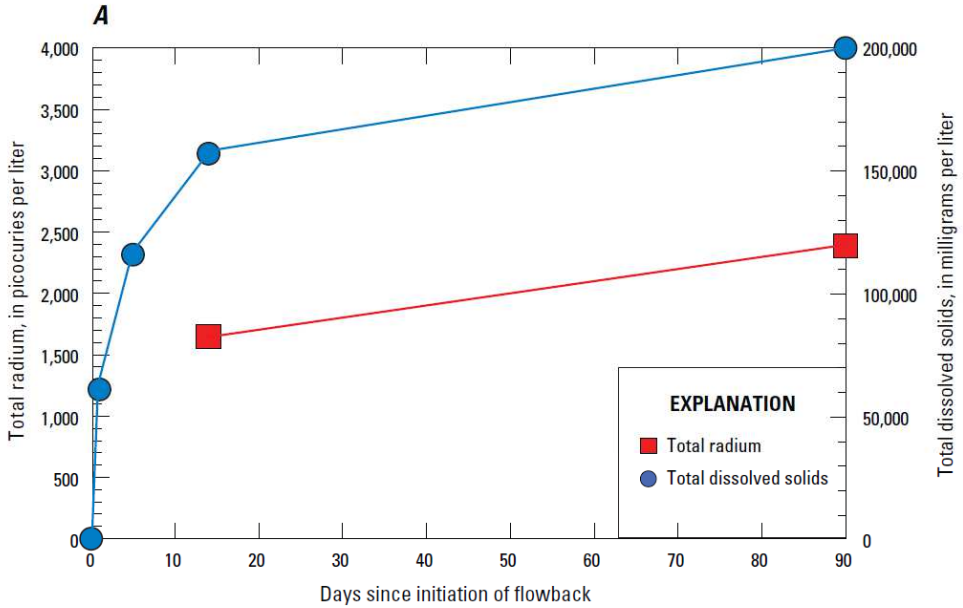
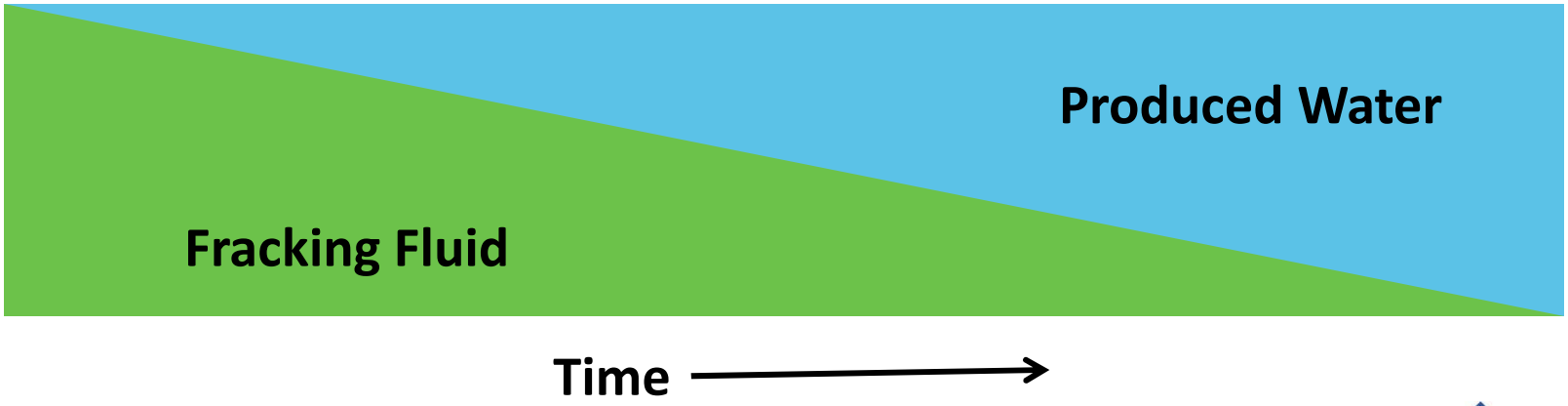
Fracking Fluids, Flowback, and Produced Water

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

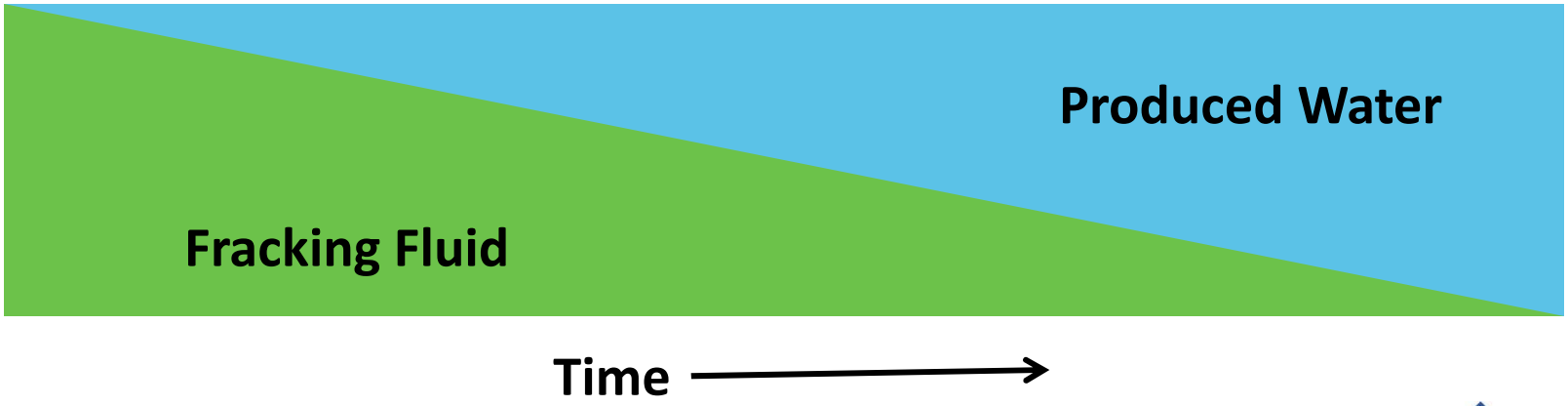


USGS, 2011

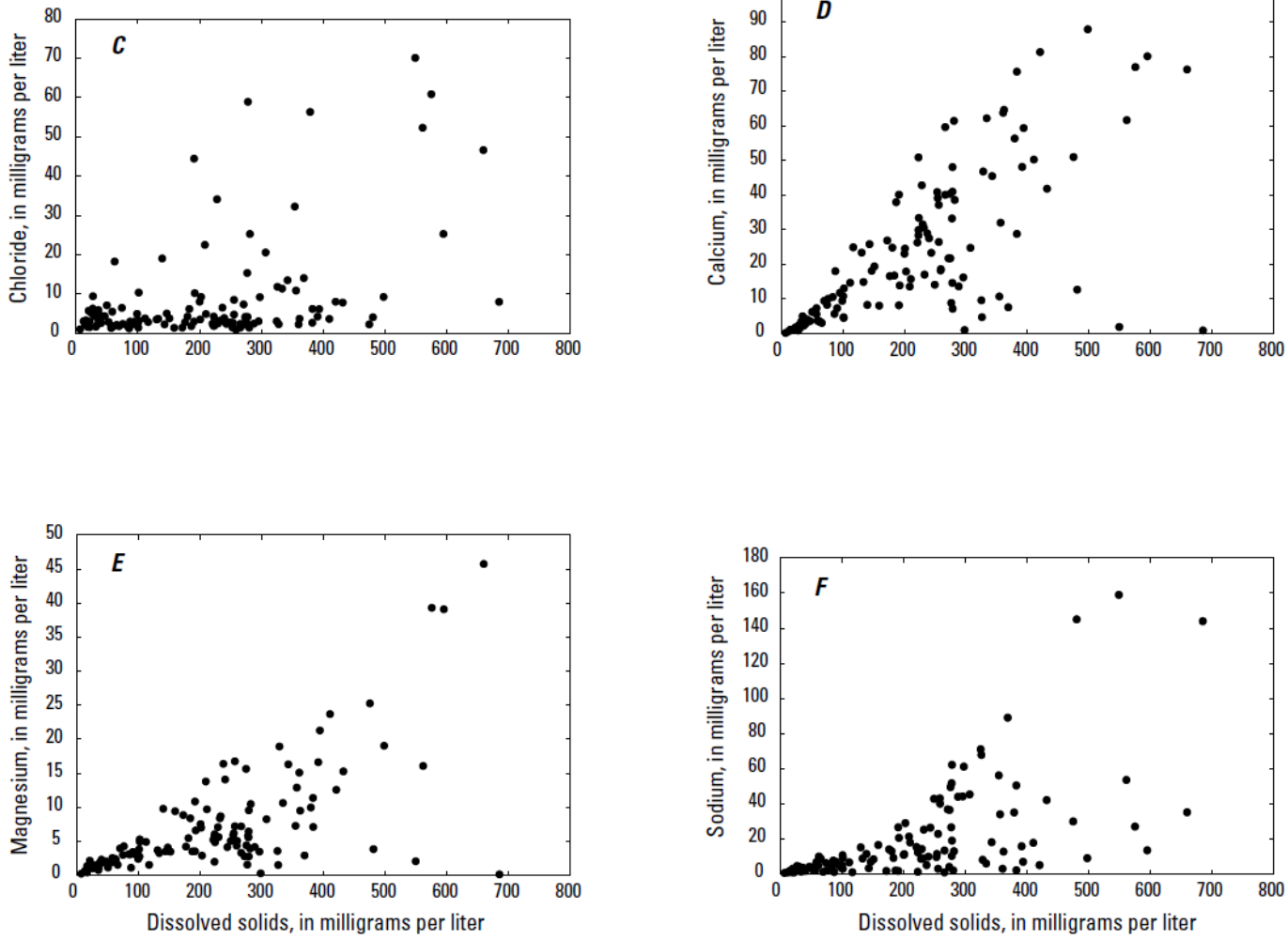


Chemical Signatures of Hydraulic Fracturing

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

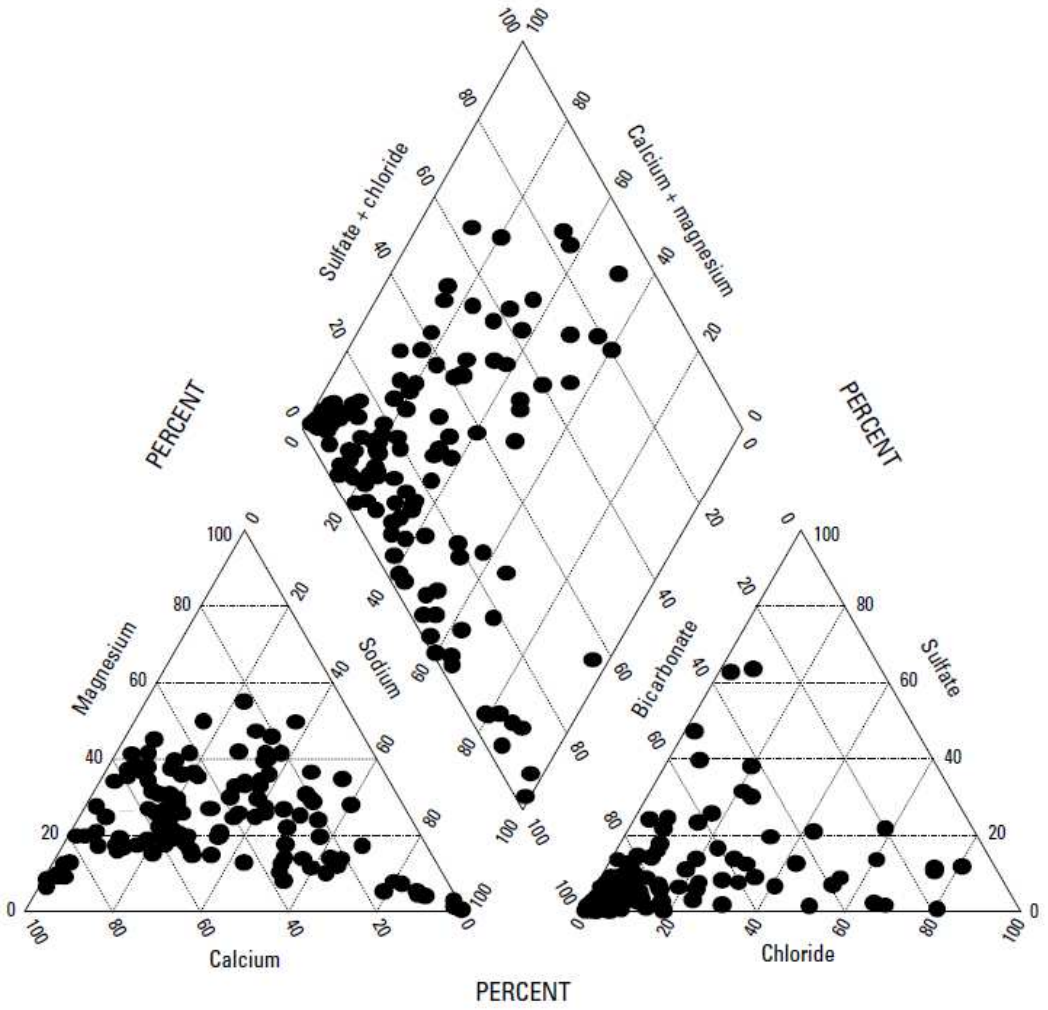


Total Dissolved Solids and Major Ions



USGS, 2012

Total Dissolved Solids and Major Ions



USGS, 2012

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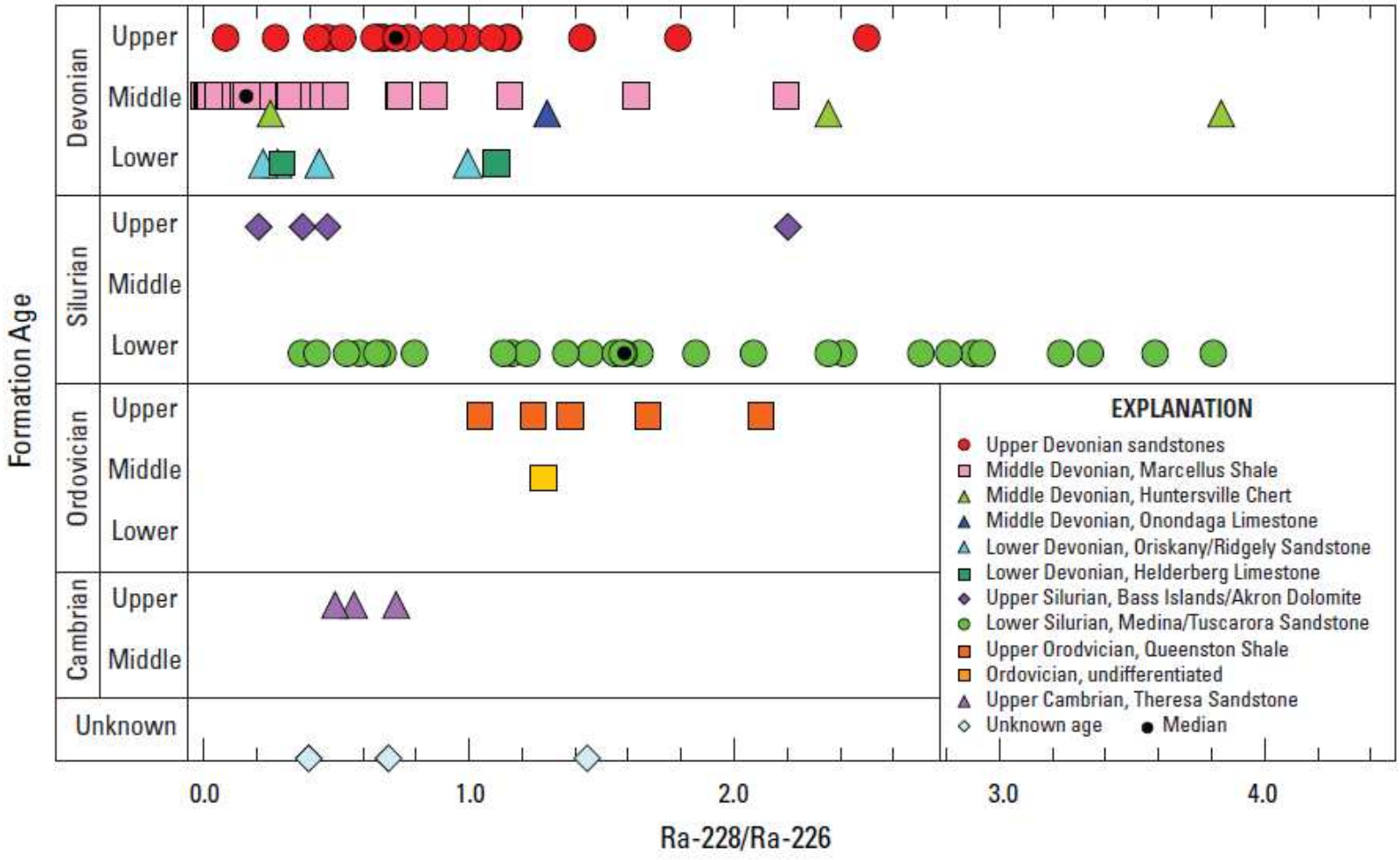
Total Dissolved Solids and Major Ions

- 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)



USGS, 2011

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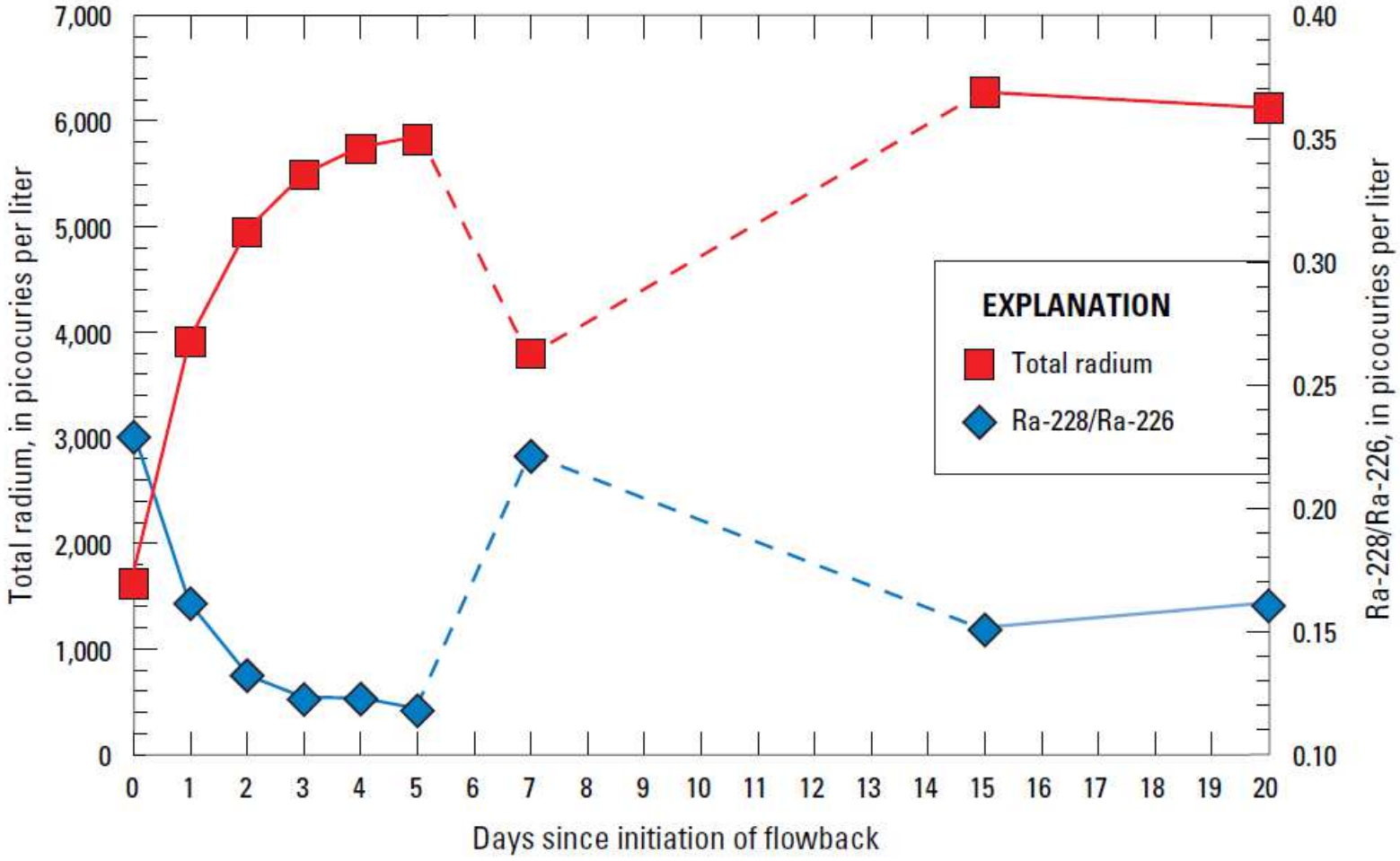
NORM (*e.g.*, radium, uranium isotopes)



USGS, 2011

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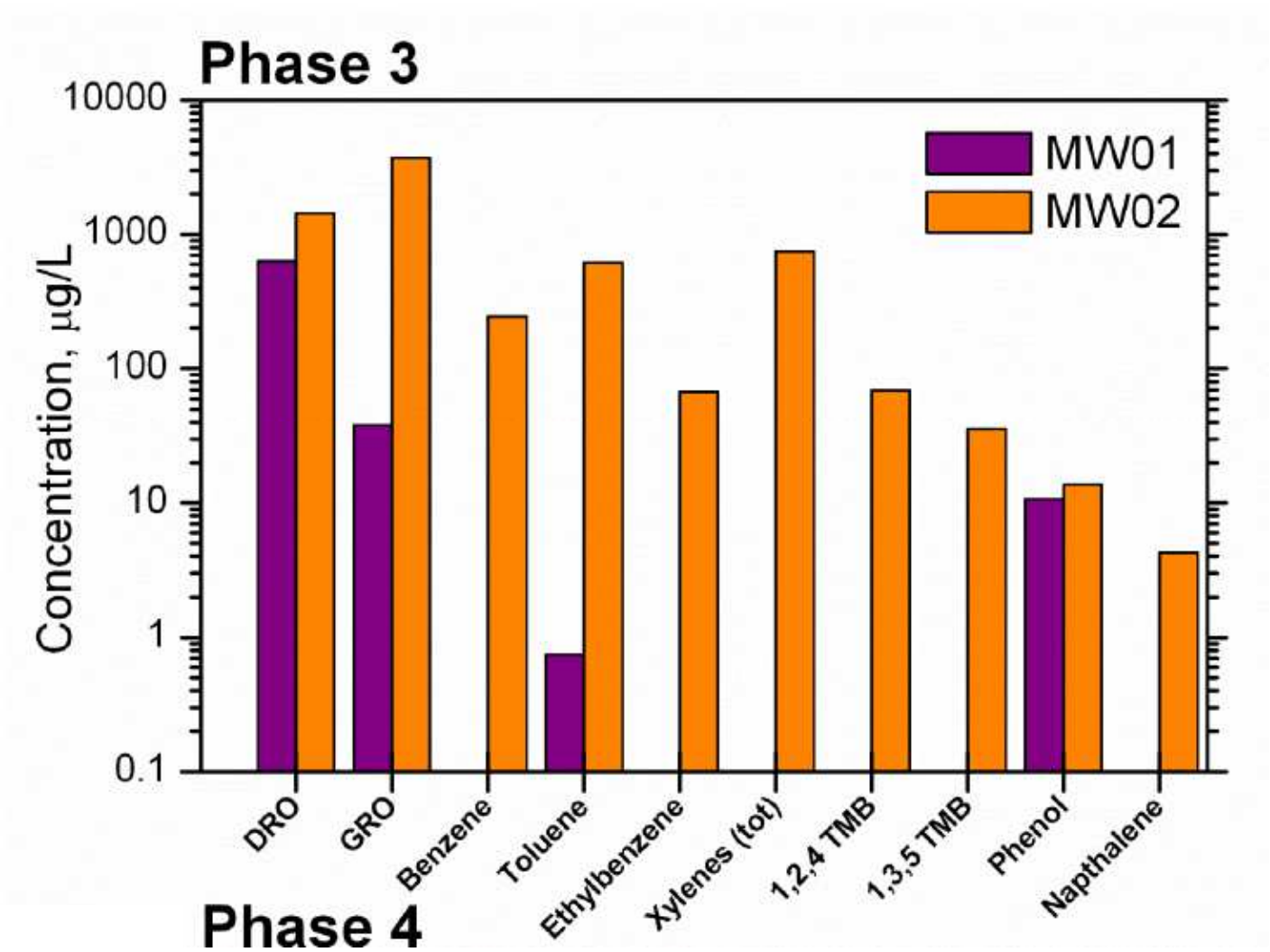
NORM (*e.g.*, radium, uranium isotopes)

- 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



US EPA, 2011

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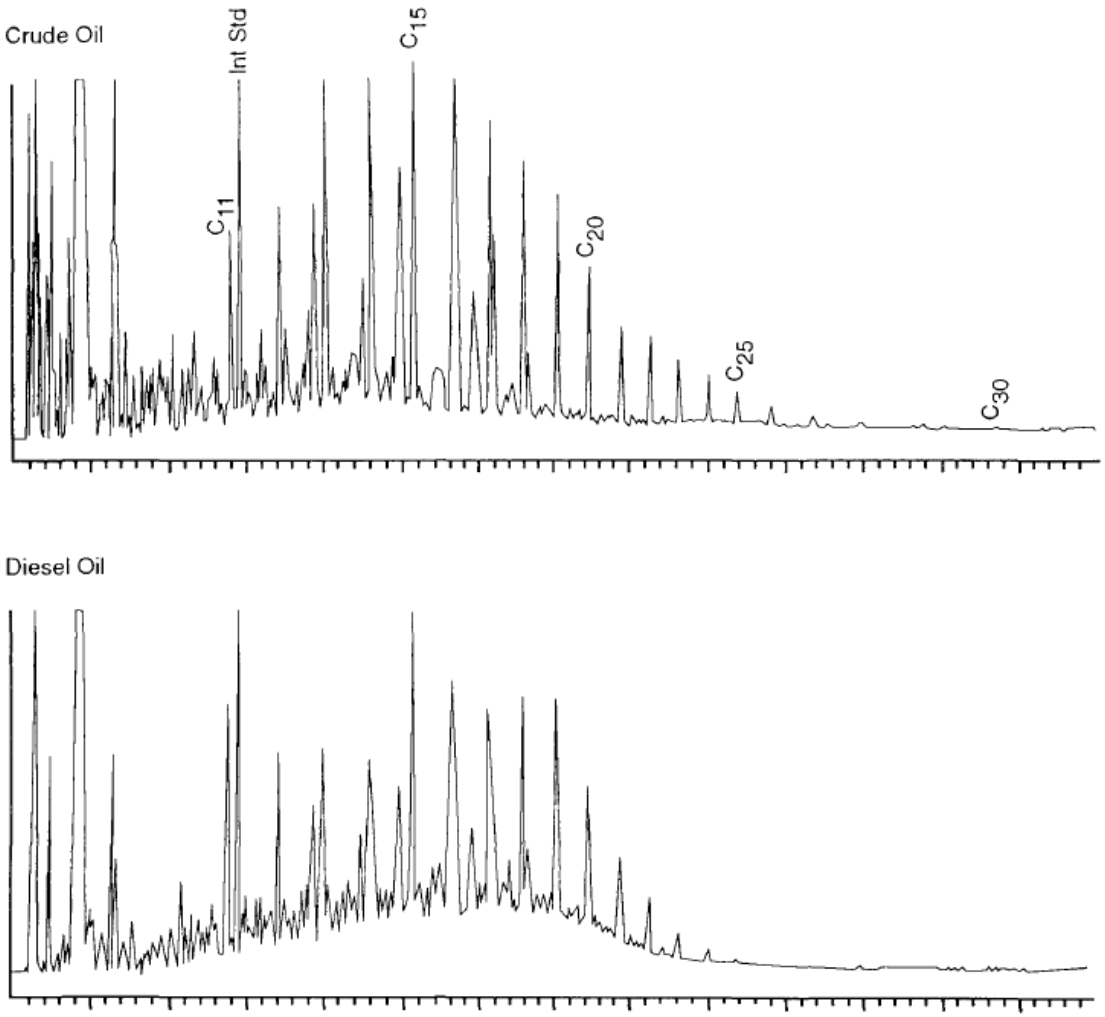
Petroleum Hydrocarbons



US EPA, 1992

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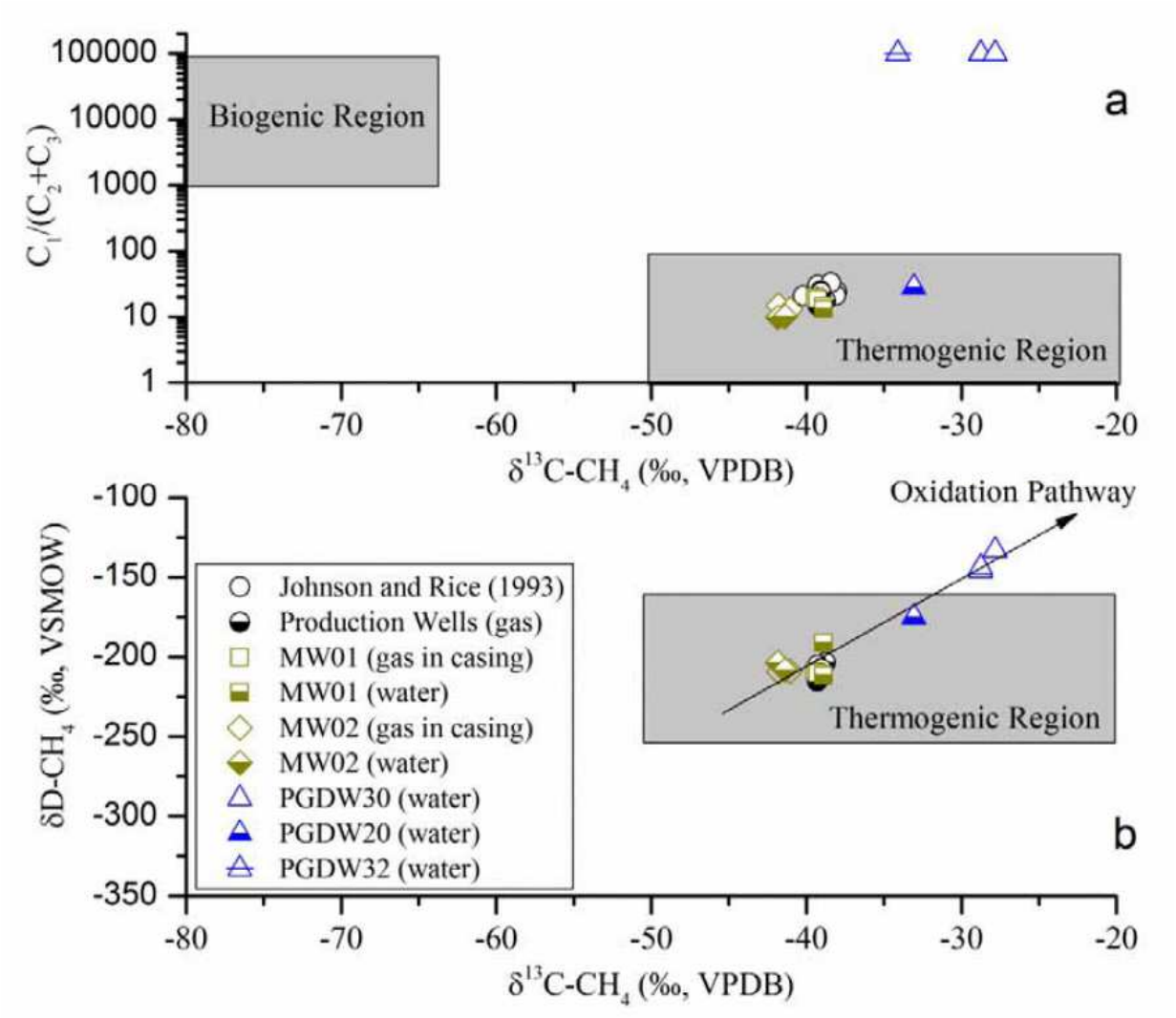
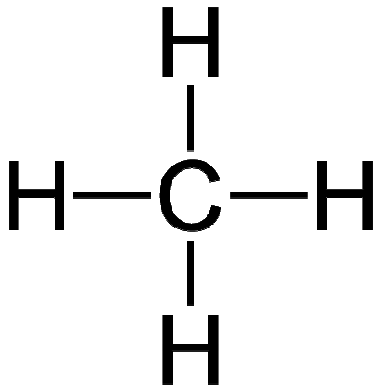
Petroleum Hydrocarbons

- 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

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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

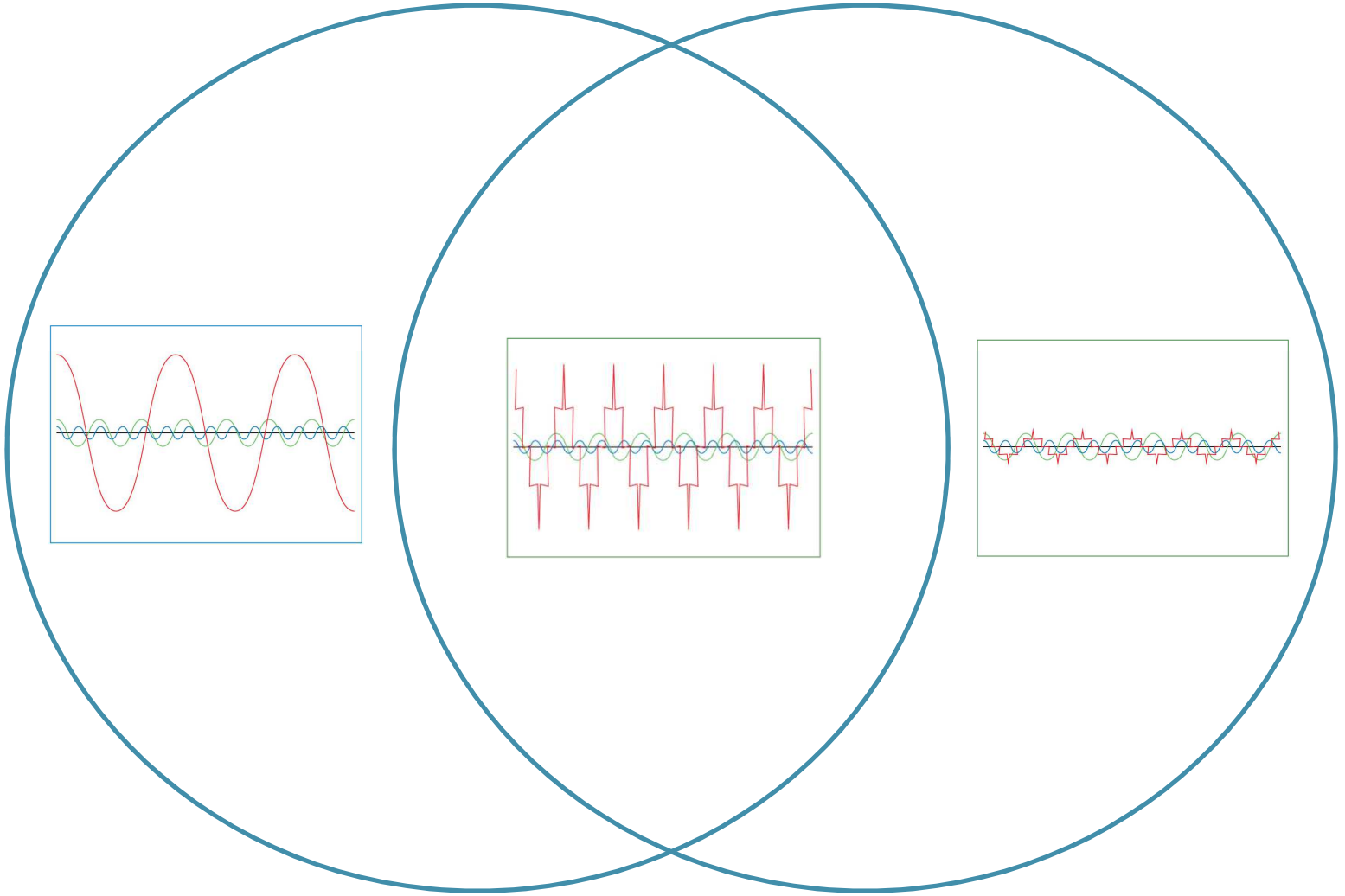
Methane Isotopes

- 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



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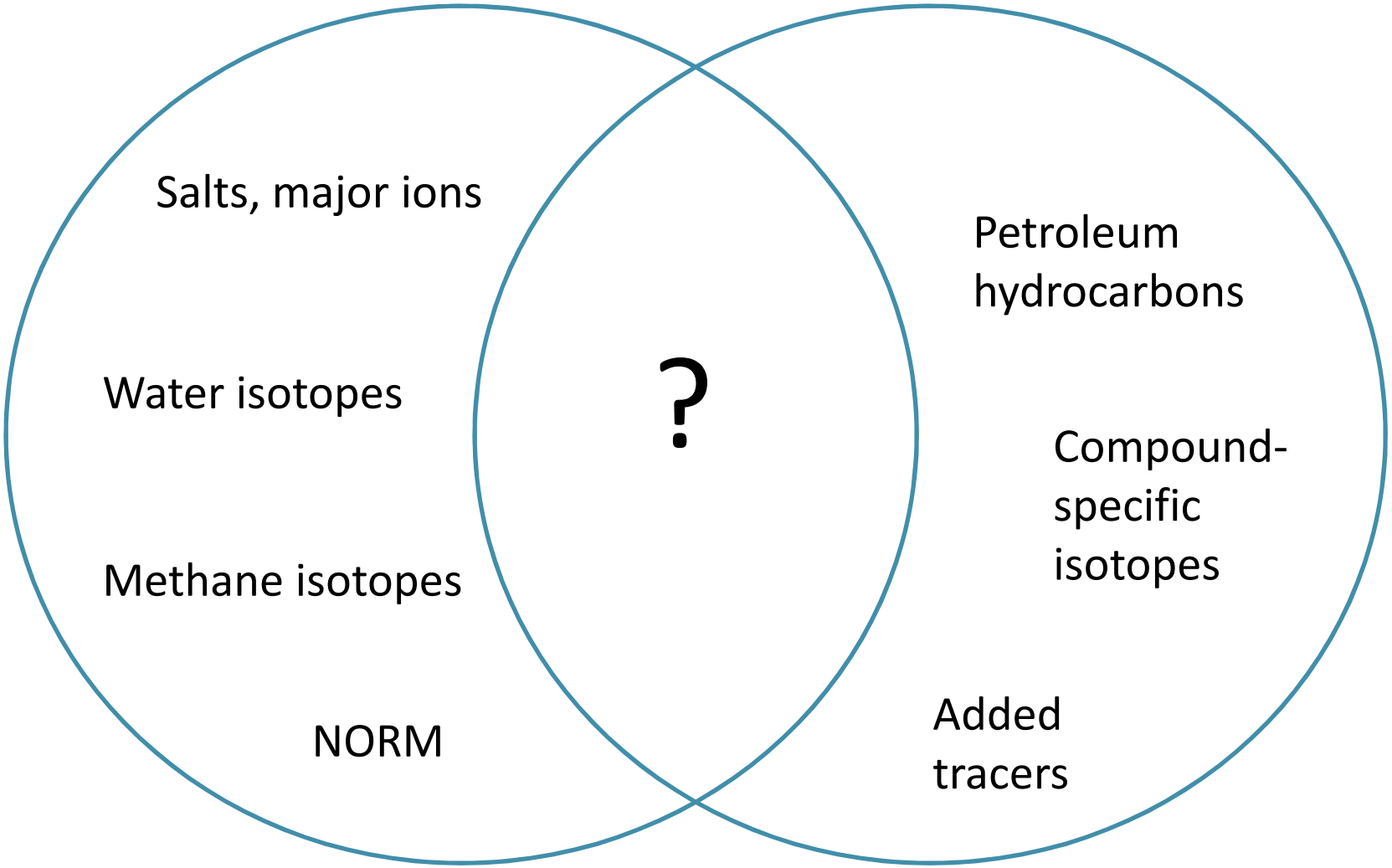
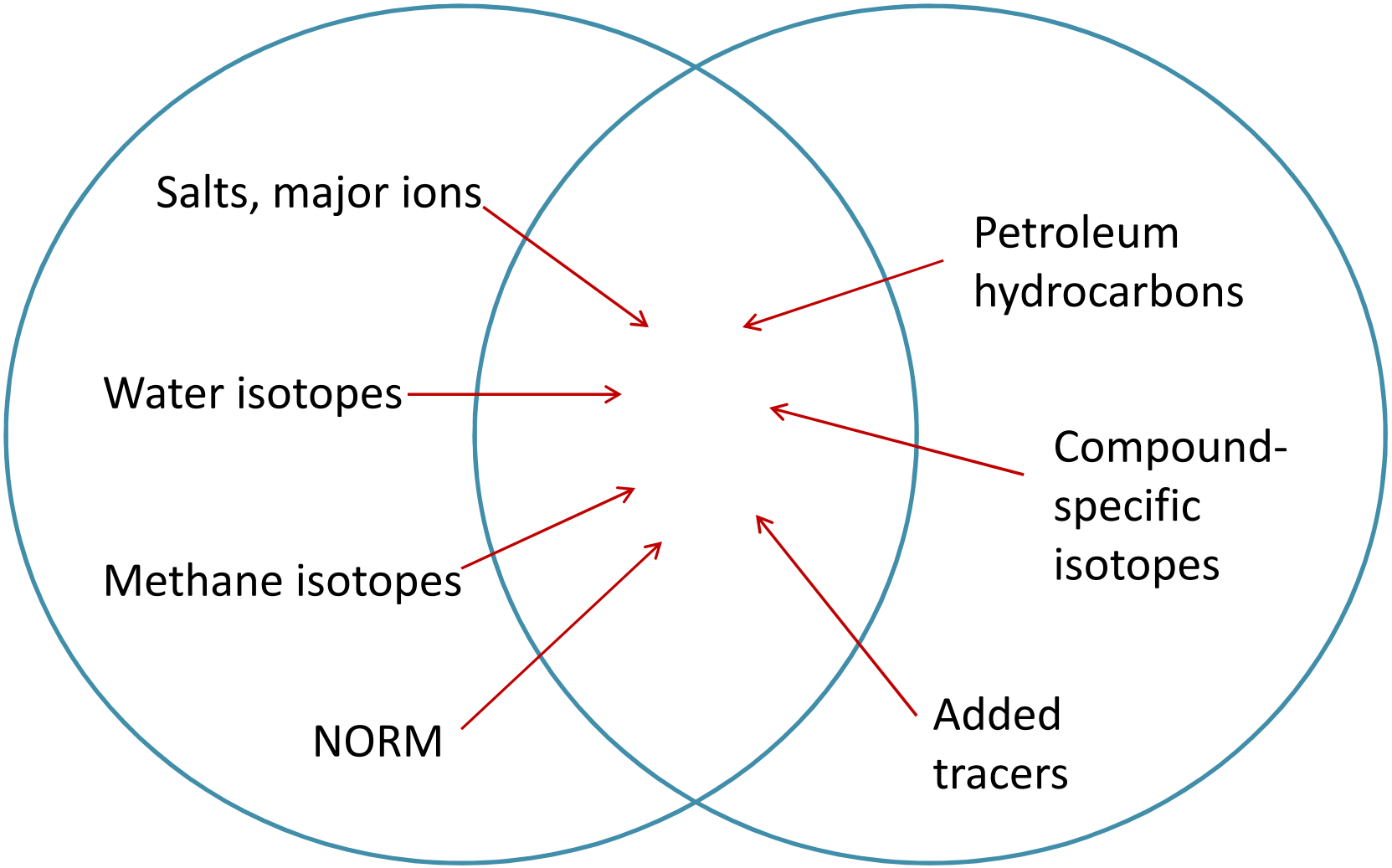
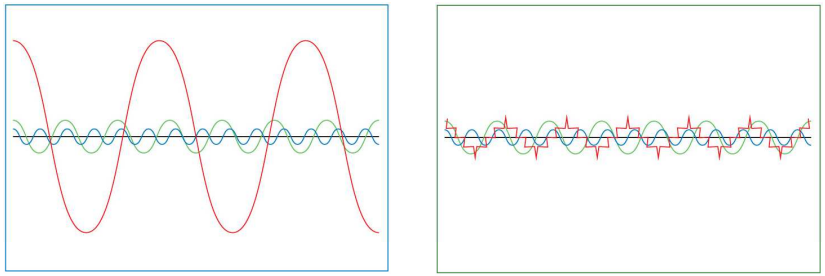
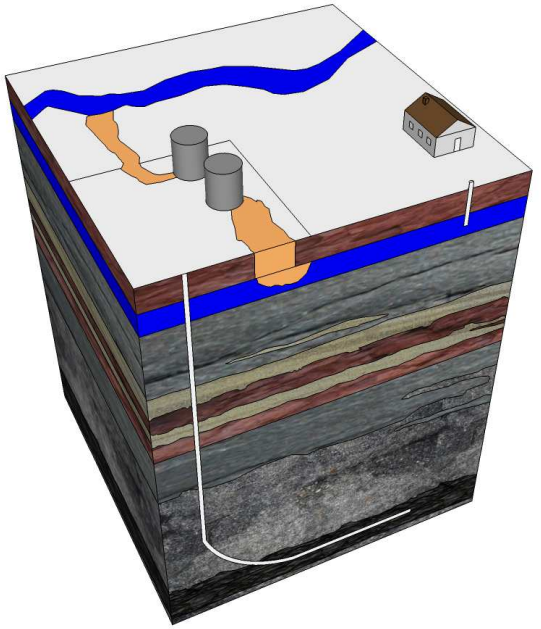


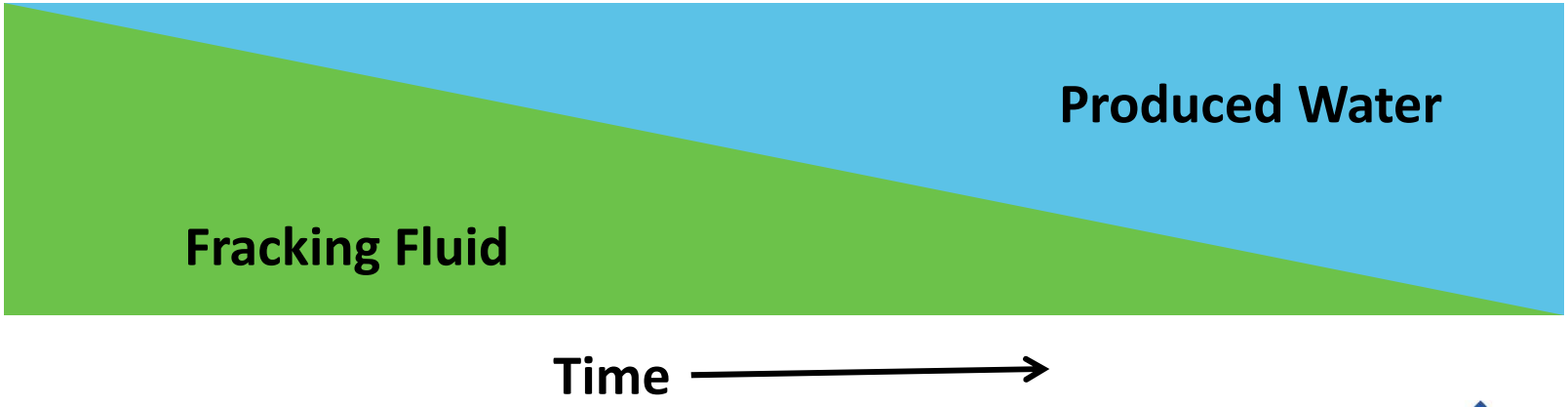
Detection *vs*. Attribution



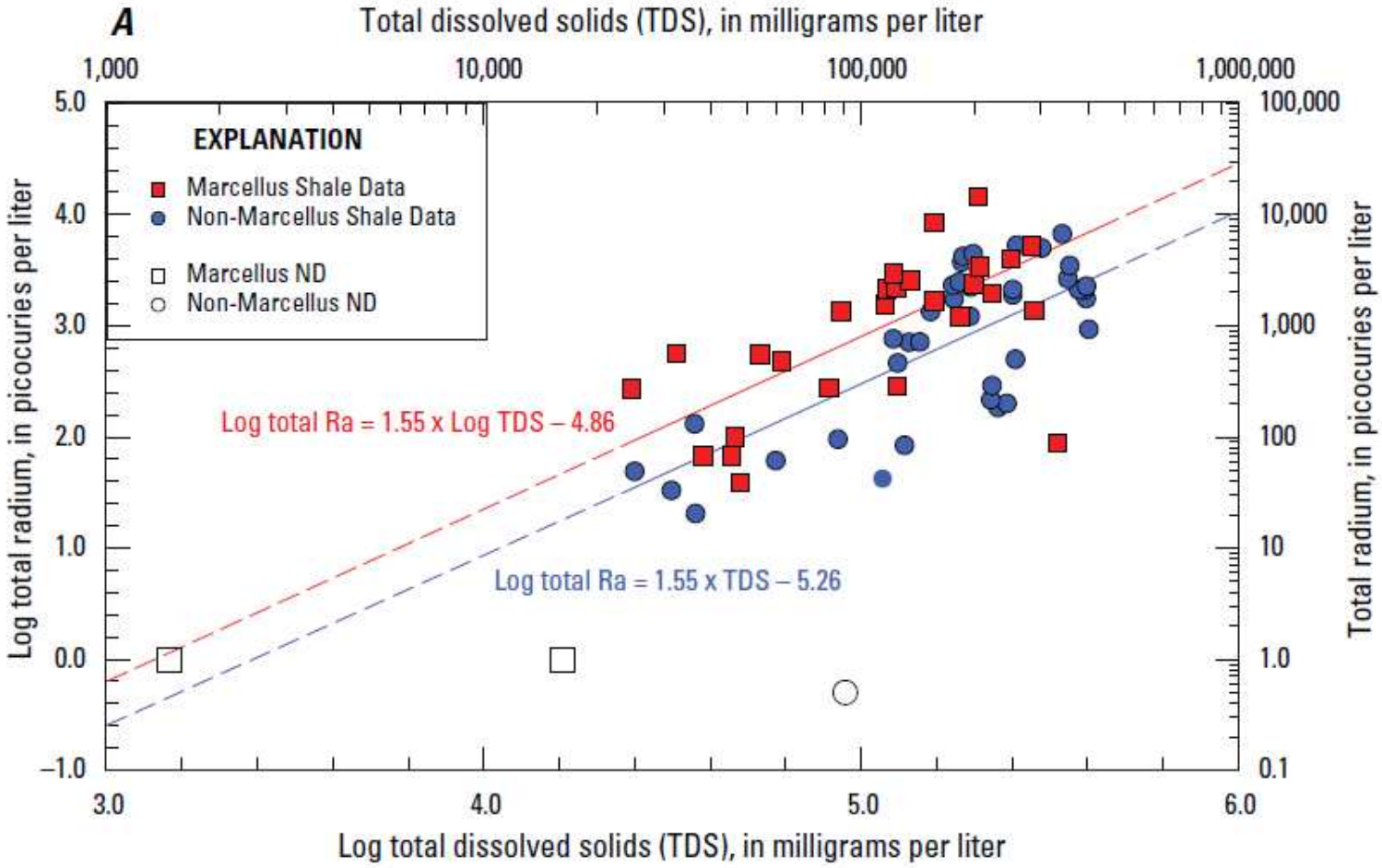
Questions?







NORM (*e.g.*, radium, uranium isotopes)



USGS, 2011

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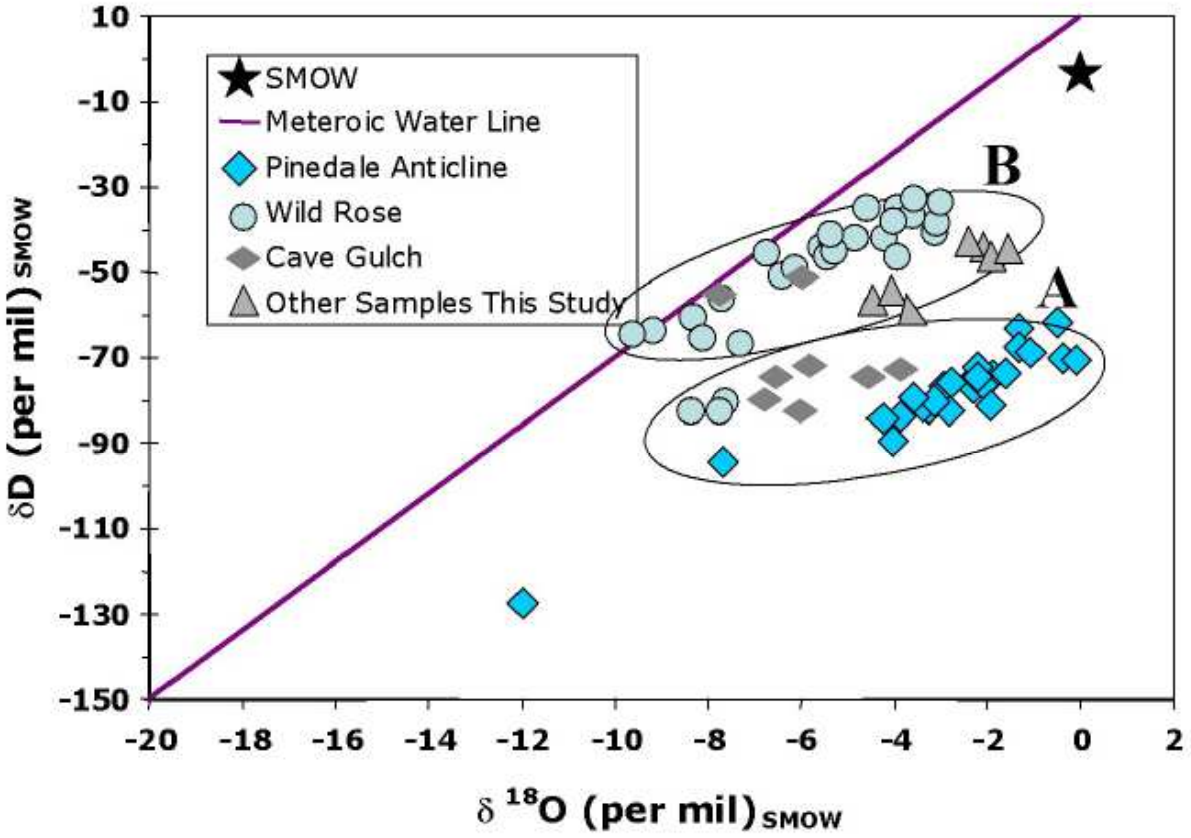
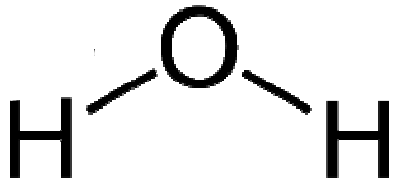
Water Isotopes



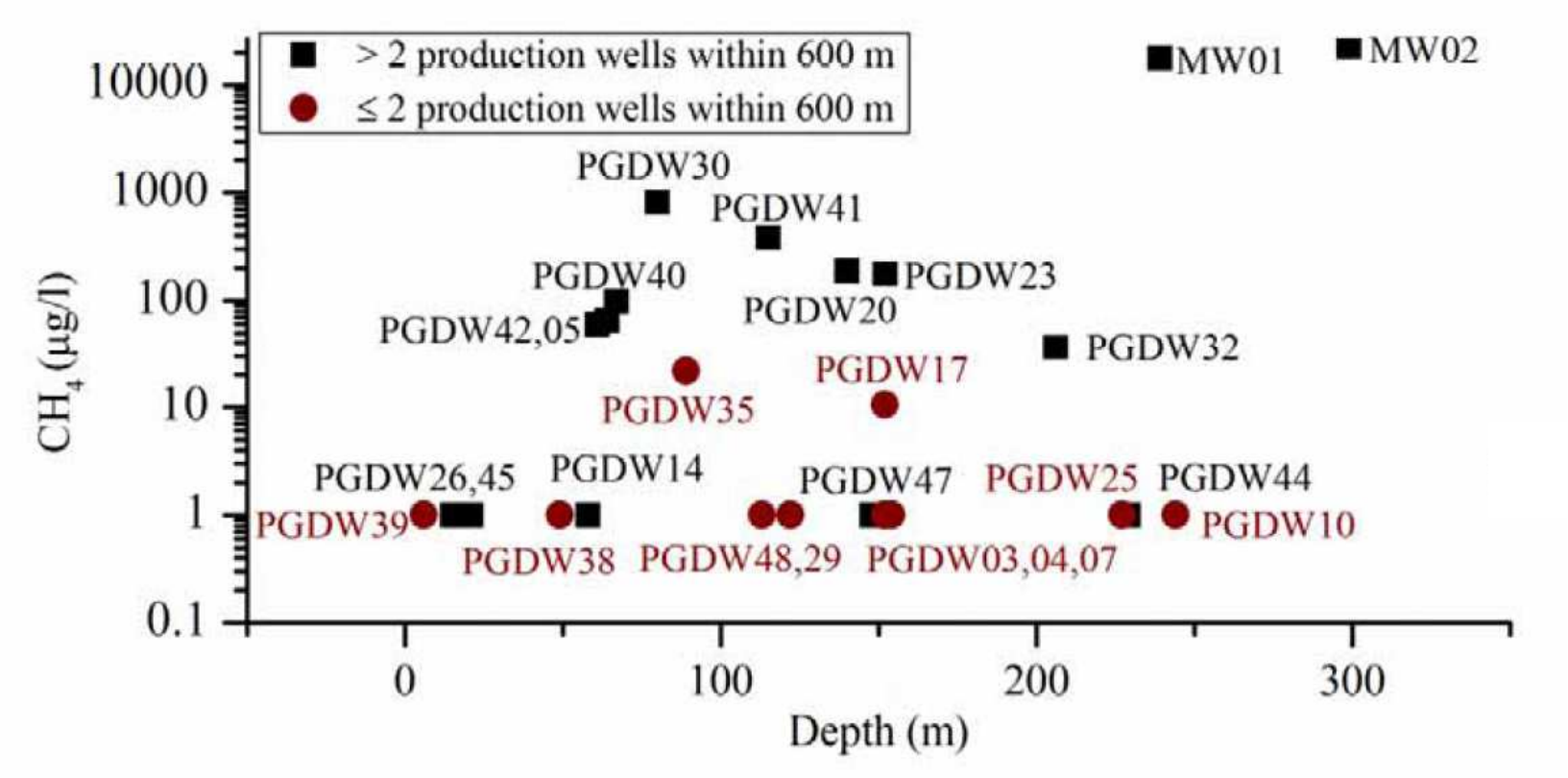


Advanced Resources International, Inc., 2005

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