Statistical and Spatial Analysis of Inorganic Anions, Cations and Radionuclides in California’s Groundwater: establishing a background and analyzing spatial variability

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Three Part Presentation

Part I: Radium & Hydraulic Fracturing

Part II: California vs. Other Oil & Gas Regions

Part III: California: Analysis of Geochemical Data Availability in Hydraulic Fracturing Areas
# Radium & Hydraulic Fracturing

<table>
<thead>
<tr>
<th><strong>18,000 pCi/L</strong></th>
<th>Max activity detected in Marcellus Shale produced waters(^1)</th>
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</thead>
<tbody>
<tr>
<td><strong>30%</strong></td>
<td>Of all Marcellus wastewater treated and discharged to local streams in 2011(^2)</td>
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<tr>
<td><strong>60 / 5 pCi/L</strong></td>
<td>EPA Industrial Effluent Discharge Limit for Radium / EPA drinking water MCL</td>
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<tr>
<td><strong>23,600 pCi/kg</strong></td>
<td>Activity in stream sediments near Pennsylvanian treatment facility effluent discharge point.</td>
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Radium Cycle in Hydraulic Fracturing

1. Deeply seated formation water is largely anoxic

2. Radium accumulates in formation waters via $^{238}\text{U}$ and $^{232}\text{Th}$ decay

3. Fractured formation rocks release radium in solution and/or on metal carriers (i.e. Barium)

4. Radium is transported to surface in produced and flowback water

$^{238}\text{U} \rightarrow ^{226}\text{Ra} \rightarrow \text{Half Life} = 1600 \text{ years; emissions} = \alpha \& \gamma$

$^{232}\text{Th} \rightarrow ^{228}\text{Ra} \rightarrow \text{Half Life} = 5.75 \text{ years; emissions} = \beta$
## Produced waters

| Cations and anions in Marcellus Shale Produced Water³ with (EPA MCL) mg/L |
|-----------------------------|-----------------------------|
| Chloride                   | 146,667 (250)               |
| Strontium                  | 36,333 (None)               |
| Sodium                     | 29,333 (None)               |
| Calcium                    | 13,000 (None)               |
| Barium                     | 9,000 (2)                   |
| TDS                        | 277,666 (500)               |

Standard EPA method for analyzing radium in drinking water (EPA 903.0) utilizes the co-precipitation of radium with chemically similar barium. EPA method 903.0 produces erroneous results due to the high salinity and elevated barium concentrations in produced water.
A large amount of research and data exists for more developed oil & gas regions in the U.S.

1. Cretaceous Maverick Basin, Eagle Ford/Austin Group, Texas
2. Devonian-Mississippian Bakken Formation, North Dakota
3. Middle Devonian Marcellus Shale, New York (A) & Pennsylvania (A’)

California’s Miocene Monterey Formation exhibits major differences from other major oil & gas regions.
Diatomite vs. Black Shale

Monterey Diatomite
- Primary reservoir rock in California’s primary oil field, Belridge Oil Field
- Porosities up to 70%
- Gels with 10 to 1000x the viscosity of slickwater injected
- Less water demand: ~1,200 acre-feet/year

Marcellus Black Shale
- Primary source rock in the Marcellus, Eagle Ford and Bakken oil plays
- Porosities between 1-11%
- Slickwater containing a friction reducer with 4x the viscosity of water injected
- Higher water demand: ~12.5 acre-feet/well/frac

Photo: CSU Long Beach @ 1.13kx
http://geology.campus.ad.csulb.edu/people/bperry/Sedimentary%20Rocks%20Tour/sedimentary%20rocks%20images/biochemical%20sedimentary%20rocks/diatomite/diatomsspiculeSEMMontFmRick.jpg

Photo: University of Rochester @ 1.47kx
http://www.optics.rochester.edu/workgroups/cml/opt307/spr11/talor/Results.html
Hydraulic Fracturing has occurred in California for decades but until recently has not been regulated.

Senate Bill No. 4

CHAPTER 313

An act to amend Sections 3213, 3215, 3236.5, and 3401 of, and to add Article 3 (commencing with Section 3150) to Chapter 1 of Division 3 of, the Public Resources Code, and to add Section 10783 to the Water Code, relating to oil and gas.

[Approved by Governor September 20, 2013. Filed with Secretary of State September 20, 2013.]
California: Hydraulic Fracturing
Data assembled from CA DOGGR and GAMA/CDPH databases utilizing R-Project Statistical Software

Dept. of Water Resources priority groundwater basins

65% Of Bakersfield’s municipal water supply is from GW

6.8 Billion dollars in agriculture revenue (2013)

21 DWR’s priority basin ranking out of 515 GW basins

Approved Well Stimulation Treatment in California

99% Of all approved WST occurs in Kern County

94% Kern County WST in Belridge and Elk Hills fields

96% WST as “Hydraulic Fracture” in Kern County
California: Hydraulic Fracturing

California
Wells = 978
Kern County = 970

Belridge Oil Field
Wells = 827
Of Total = 85%

Elk Hills Oil Field
Wells = 88
Of Total = 9%

Other Kern County Oil Fields
Wells = 55
Of Total = 5%

Data from CA Division of Oil, Gas and Geothermal Resources (DOGGR)
California: Hydraulic Fracturing & Radium

**Radium-226**
- Data pts. = 164
- CDPH pts. = 93%
- Mean = 0.321
- Median = 0.180
- Data pts. near WST = 0-1

**Radium-228**
- Data pts. = 275
- CDPH pts. = 96%
- Mean = 0.703
- Median = 0.440
- Data pts. near WST = 3-4

**Data from CA Groundwater Ambient Monitoring & Assessment Program (GAMA)**
California: Hydraulic Fracturing & Total Diss. Soil Solids

TDS (mg/L)
Data pts. = 5074
CDPH = 64%

Mean = 1461
Median = 285

EPA Drinking Water MCL = 500 mg/L

Protected Water <10,000 ppm
Conclusions and Further Research

• Produced waters contain elevated radium activity and high concentrations of other anions and cations, including TDS.

• The Monterey Formation presents a very different geologic setting and geochemical indicators will likely be different from previously studied WST areas.

• Too little data are available to interpret the relationship between ambient groundwater conditions and WST in Kern County.

• In order to use geochemical data to examine effects of WST on shallower groundwater, data from oil field shallow groundwater and WST wastewater, produced and flowback are needed.
References


