Field Studies to Assess Biostimulation for Remediation of Radionuclides and Heavy Metals at an *in situ* Leach Mine Site

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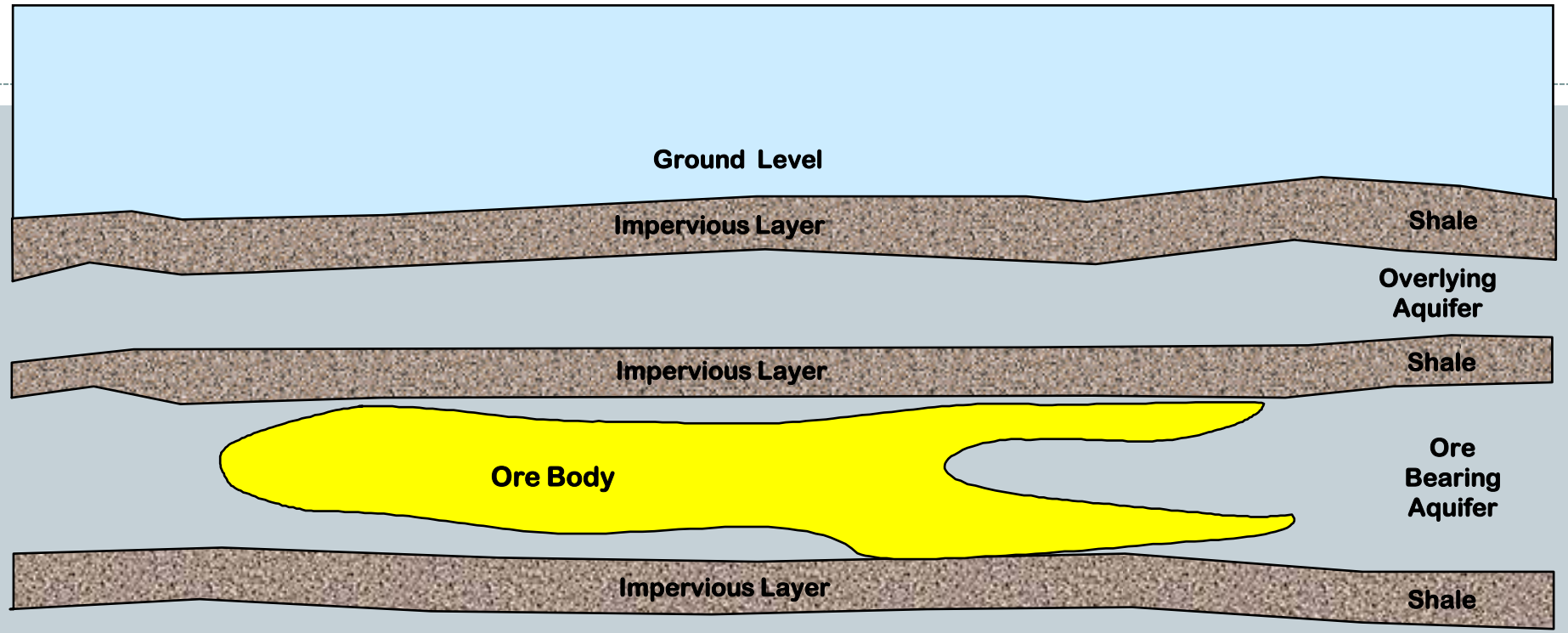
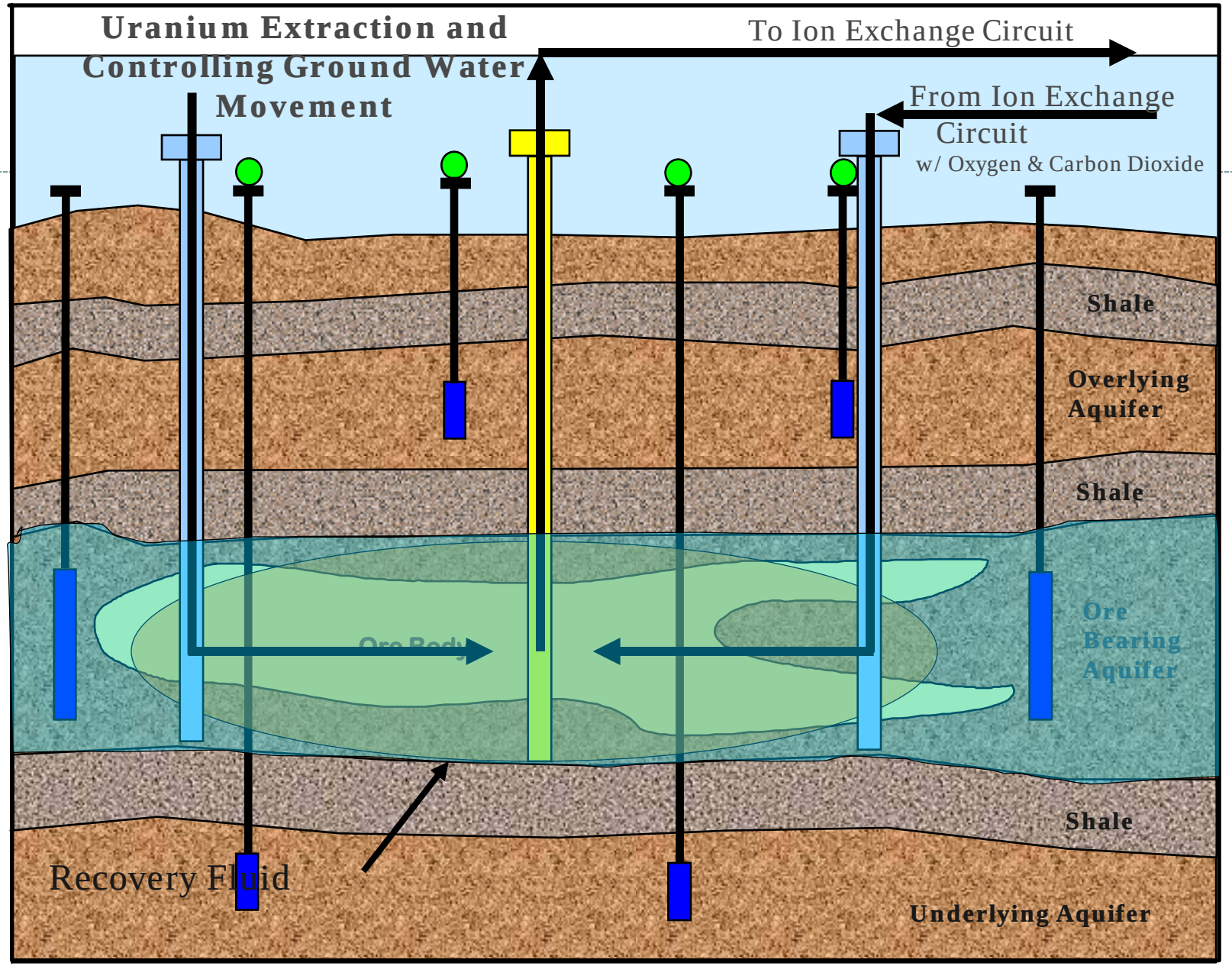
Geology and Wellfield Development



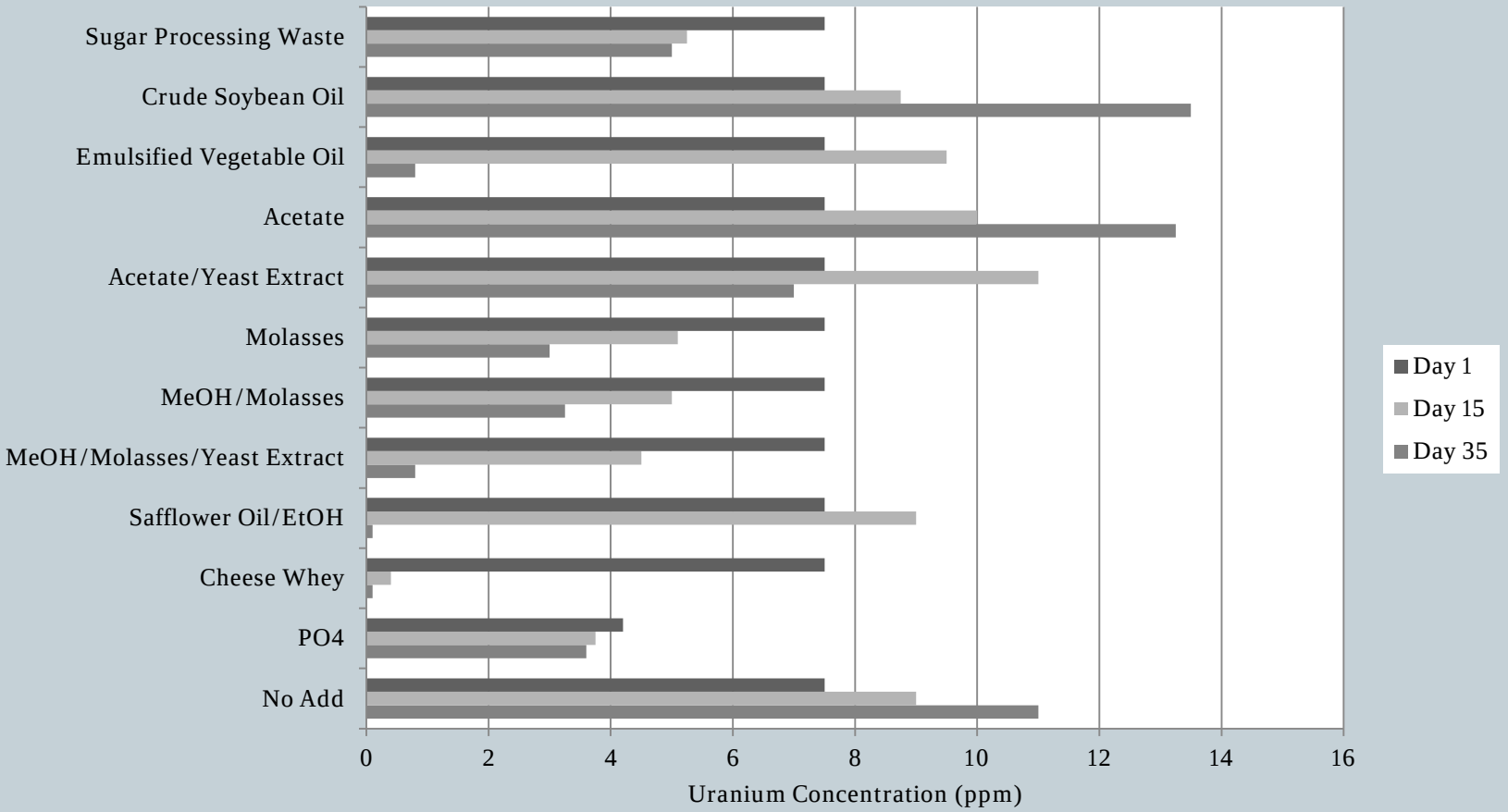
- The ore occurs at depths of several hundred feet, the extent is determined by surface drilling.
- Ore is typically confined by impervious shale.
- After deposit delineated, an extraction plan is prepared and grids of injection and production wells are installed.


Uranium Extraction and Controlling Ground Water Movement
To Ion Exchange Circuit
From Ion Exchange Circuit
w/ Oxygen & Carbon Dioxide
Shale
Overlying Aquifer
Shale
Ore Body
Ore Bearing Aquifer
Shale
Recovery Fluid
Underlying Aquifer

Traditional Restoration Strategies

- Reverse Osmosis Water Sweeps
  - Remove extra mining lixiviant, TDS
  - Remove some Uranium (VI)
- Chemical Treatments
  - Attempt to reestablish reducing environment
    - i.e. Hydrogen Sulfide or Sodium Sulfide
- Very expensive, large consumptive water loss
- Evidence of rebound after treatment-U not valence reduced
- Can bio-stimulation improve the efficiency of restoration?

Previous Smith Ranch Highland Trial

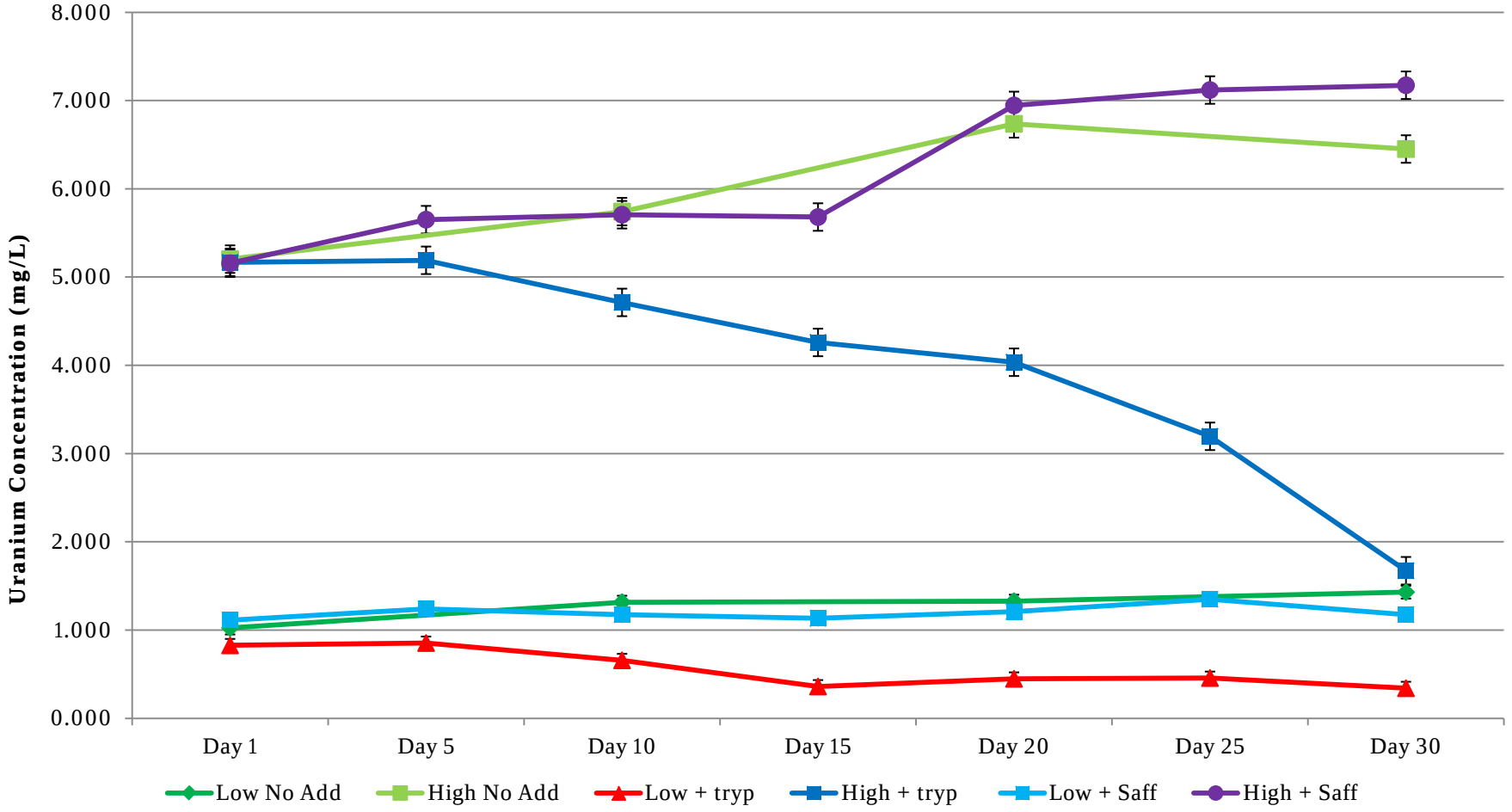


(Adapted from Hatzinger, 2004)

Microcosm Experiment Objectives

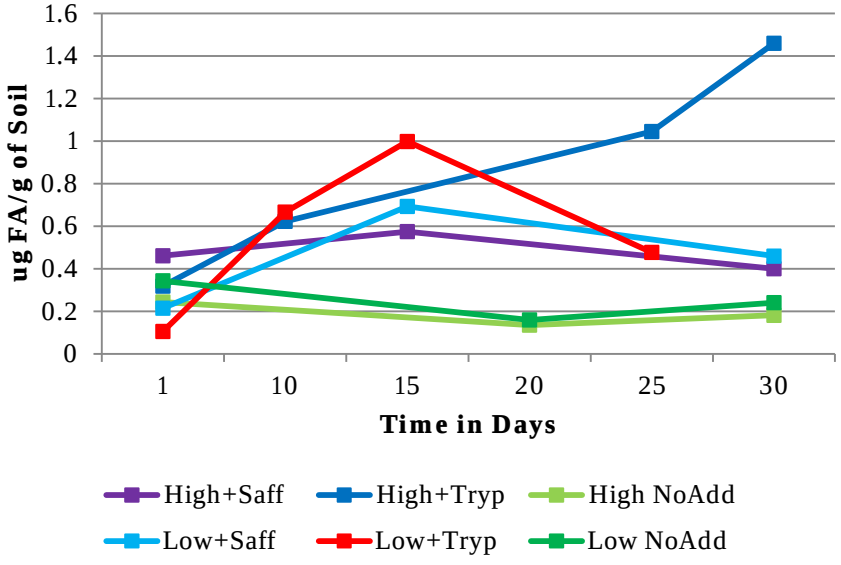
- Examine potential biostimulants for their efficacy in promoting biological reduction of Uranium (VI) in SRH system
  - Tryptone
  - Safflower oil with Methanol
- Determine effective measurements to demonstrate biological reducing situations
  - Water chemistry analyses
  - Carbon-isotopic analyses
  - Uranium-isotopic analyses
  - Microbial community analyses

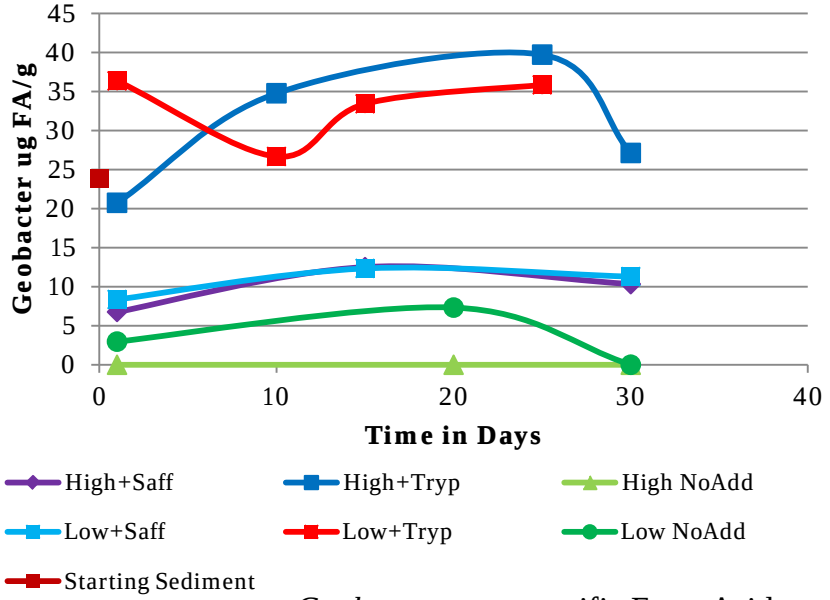
Soluble Uranium Results



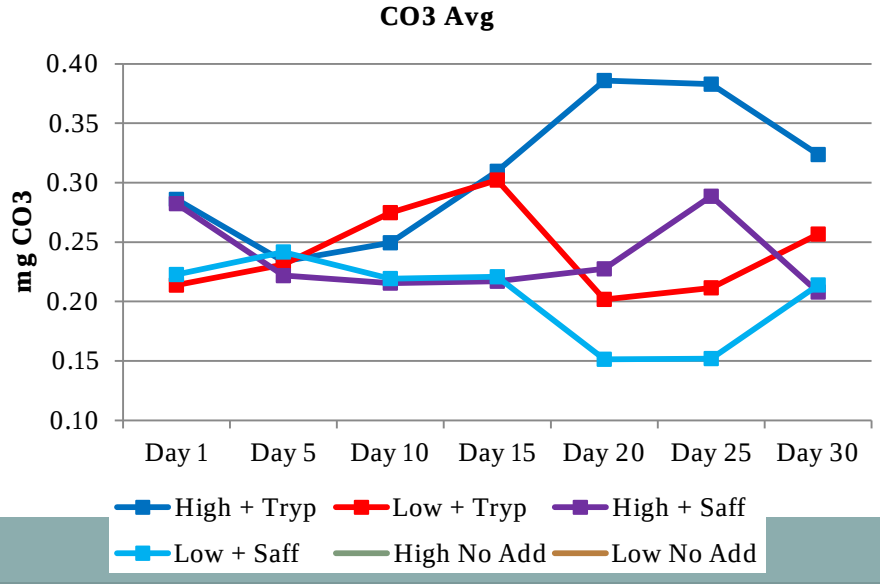
*53% reduction in Low + Tryp; 68% reduction in High + Tryp

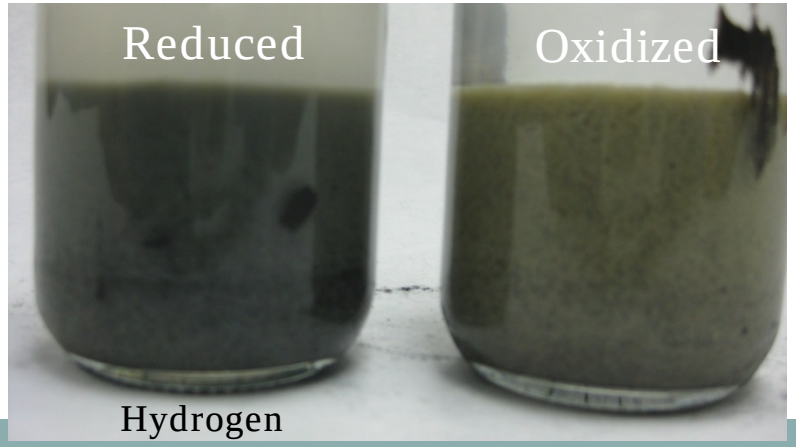
Evidence of Microbial Activity





Geobacter spp. specific Fatty Acids
15:0 iso; 16:1 w7c; 16:0

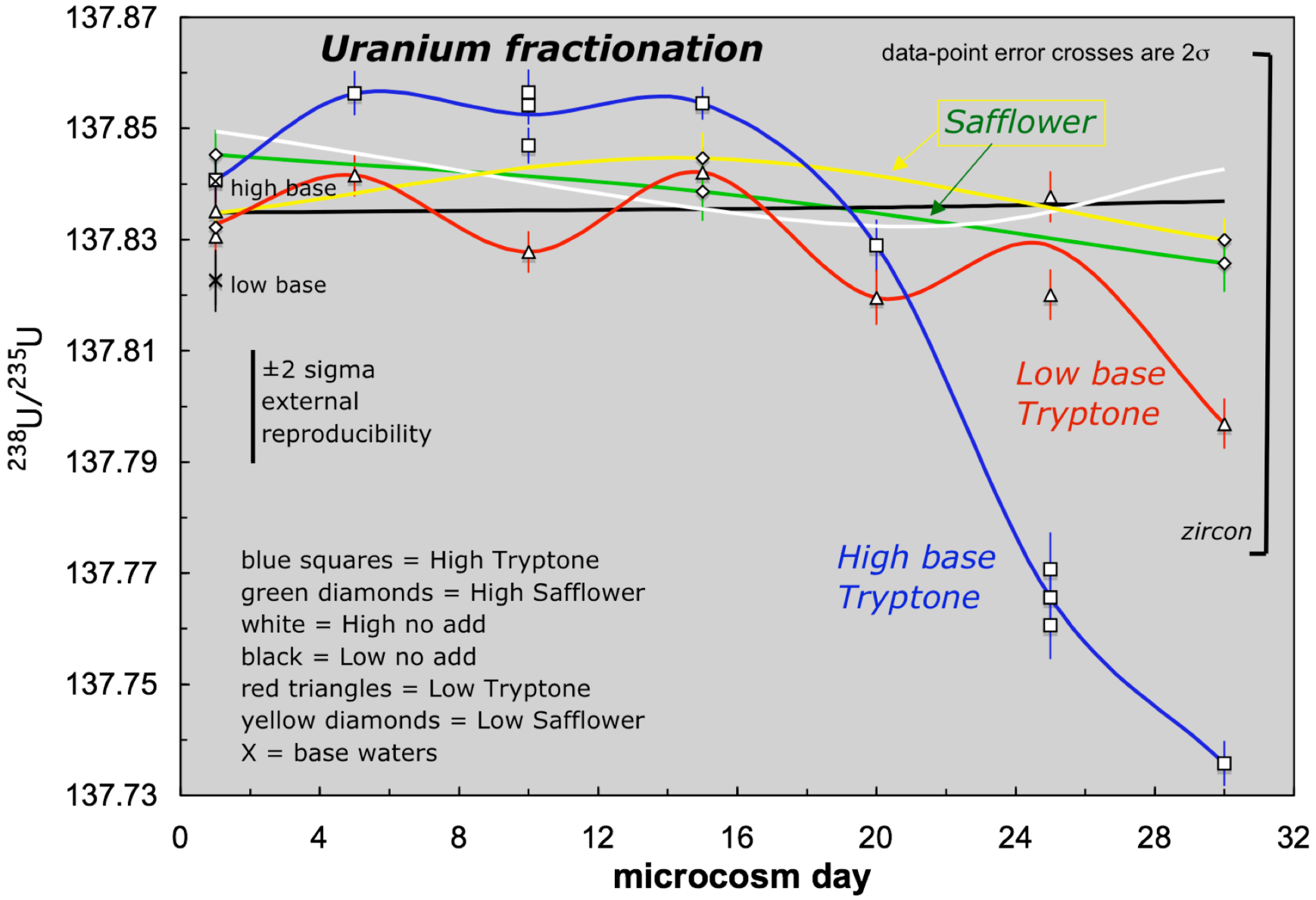




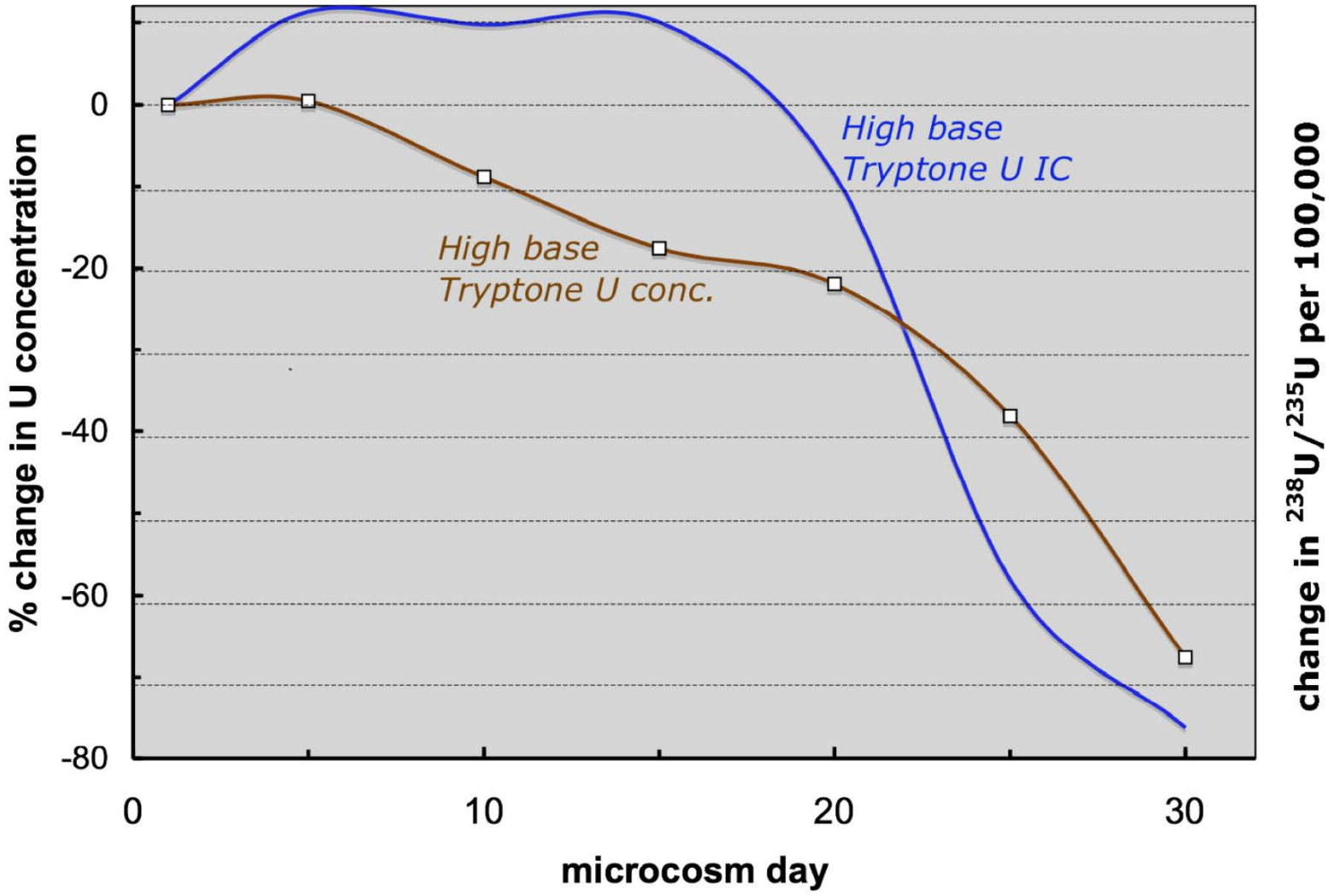
Hydrogen Sulfide Odor

Uranium Isotope Analysis Methods

- Isotopic fractionation correlates to valence reduction
- Samples of monitoring waters
- Sample load ~100 nanograms (10^{-9} gm) U
- Spiked with $^{233}U/^{236}U$ tracer
- Purification on ion exchange columns
- Sample/blank ~10,000
- Multi-collector, inductively-coupled plasma, mass spectrometry (MC-ICP-MS)


Uranium fractionation
data-point error crosses are 2σ
Safflower
high base
low base
±2 sigma
external
reproducibility
Low base
Tryptone
High base
Tryptone
zircon
blue squares = High Tryptone
green diamonds = High Safflower
white = High no add
black = Low no add
red triangles = Low Tryptone
yellow diamonds = Low Safflower
X = base waters
238U/235U
137.87
137.85
137.83
137.81
137.79
137.77
137.75
137.73
0
4
8
12
16
20
24
28
32
microcosm day

U concentration and isotopic fractionation-High Tryptone



Other Issues/Unanswered Questions from Microcosm Study

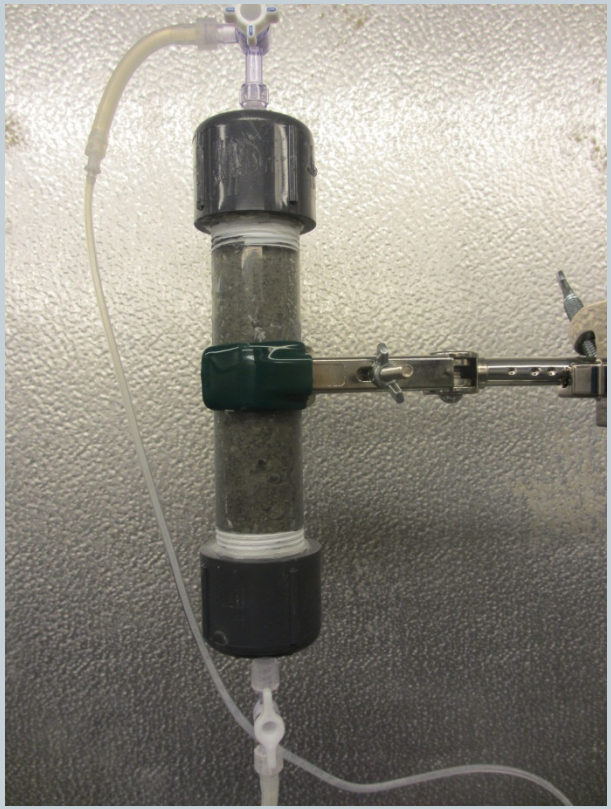
- How much tryptone is required to stimulate growth and reduction of uranium (VI)?
- Where in mining process would this type of biostimulation be the most beneficial?
- Do the monitoring metrics hold up in a continuous flow system?

Column Study Design

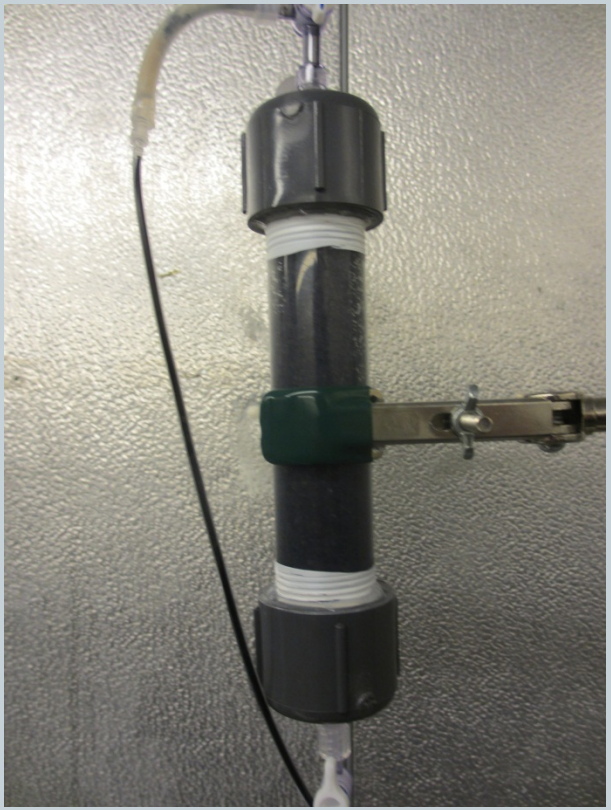
- Study was setup in a 4x4 system
  - 4 levels of tryptone stimulation
    - 2000 mg/L
    - 200 mg/L
    - 20 mg/L
    - No tryptone control (No Add)
  - 4 types of water
    - High TDS/U (7-8 ppm U)
    - Medium TDS/U (2-3 ppm U)
    - Low TDS/U (~1 ppm U)
    - Deionized control
- 16 total columns – 4 per syringe pump

Visually Observable Changes

Oxidized

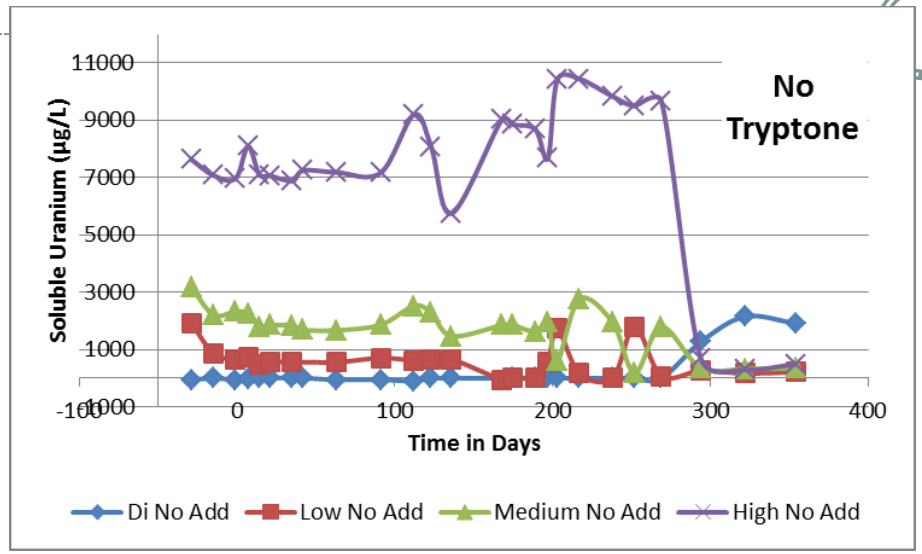


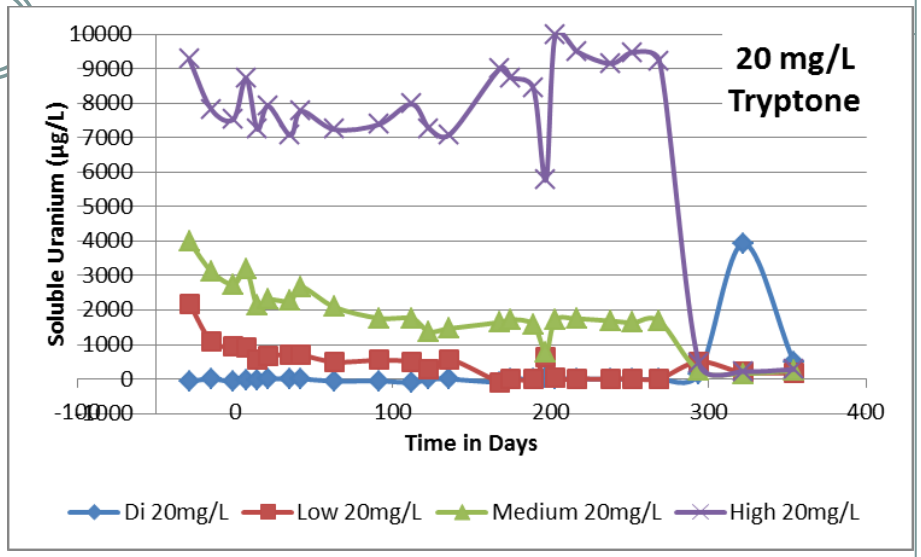
Reduced

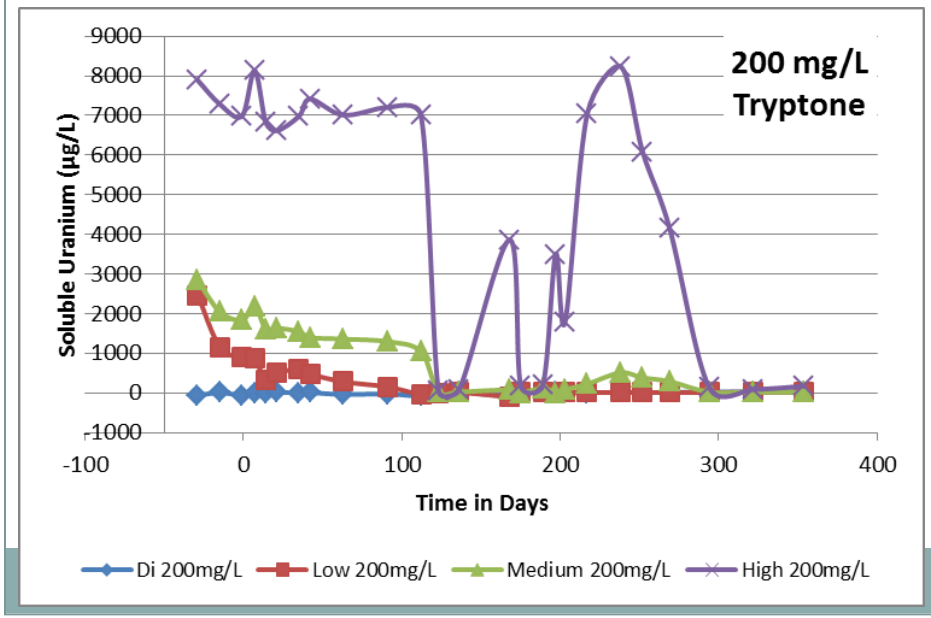


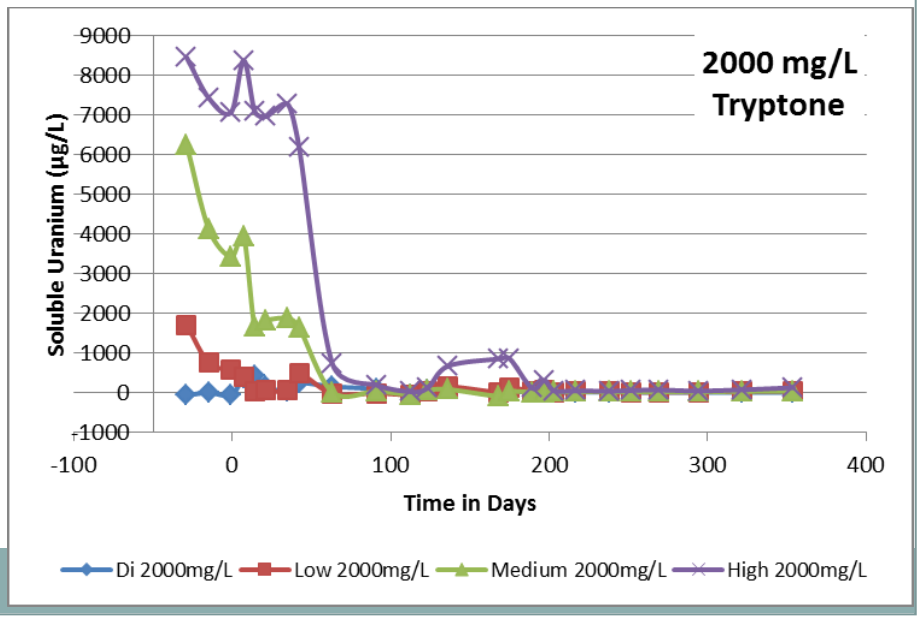
*44.4 mL average pore volume

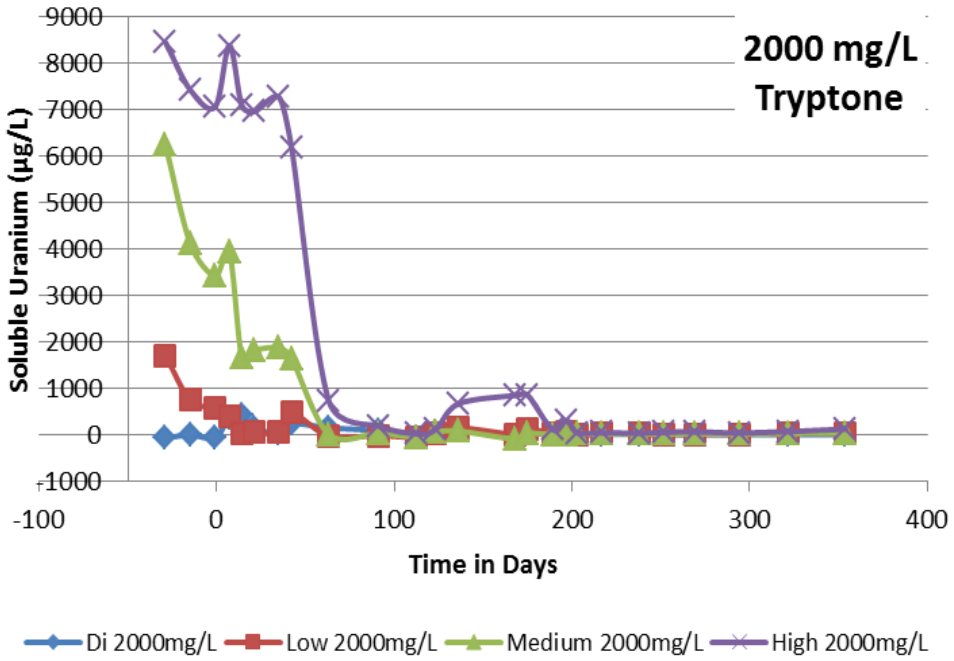
Soluble Uranium Concentration Results





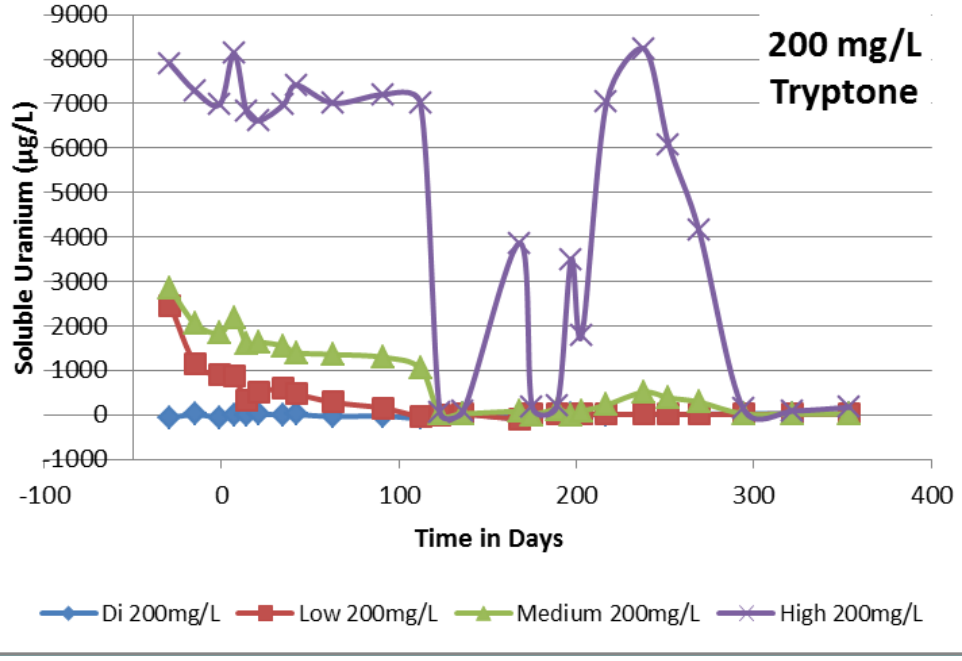






2000 mg/L Treatment

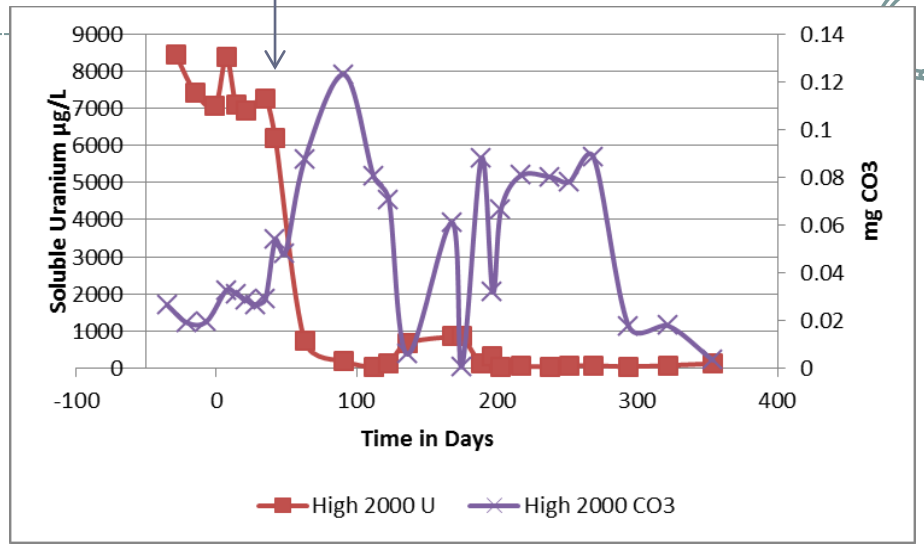
- 99.3% reduction in High 2000 treatment
- Consistent reduction beginning at ~Day 42
- Synchrotron data demonstrates high U(IV) presence in sediment

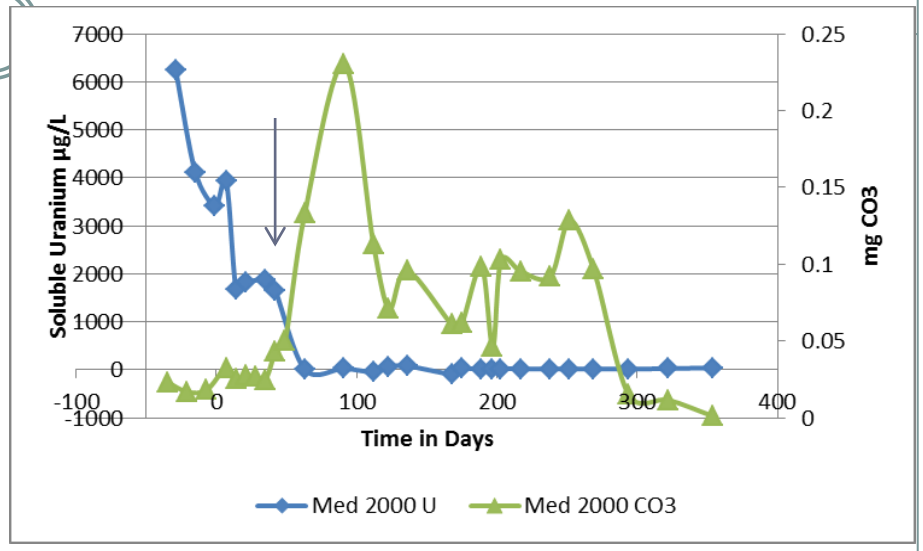


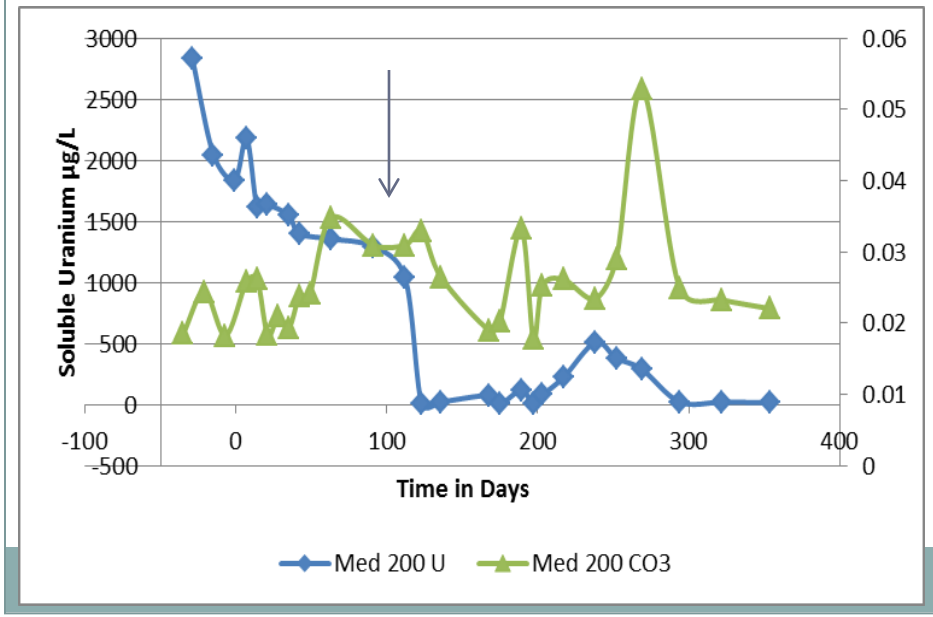
200 mg/L Treatment

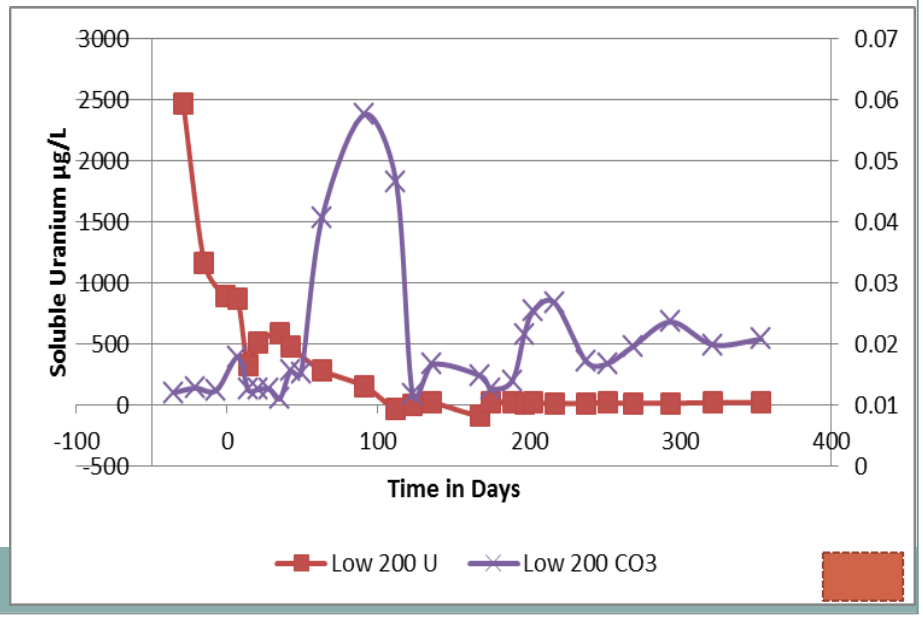
- 82.6% reduction in Medium 200 treatment
  - Beginning at ~Day 112
- Despite initial reduction, clear rebound in High TDS/U water

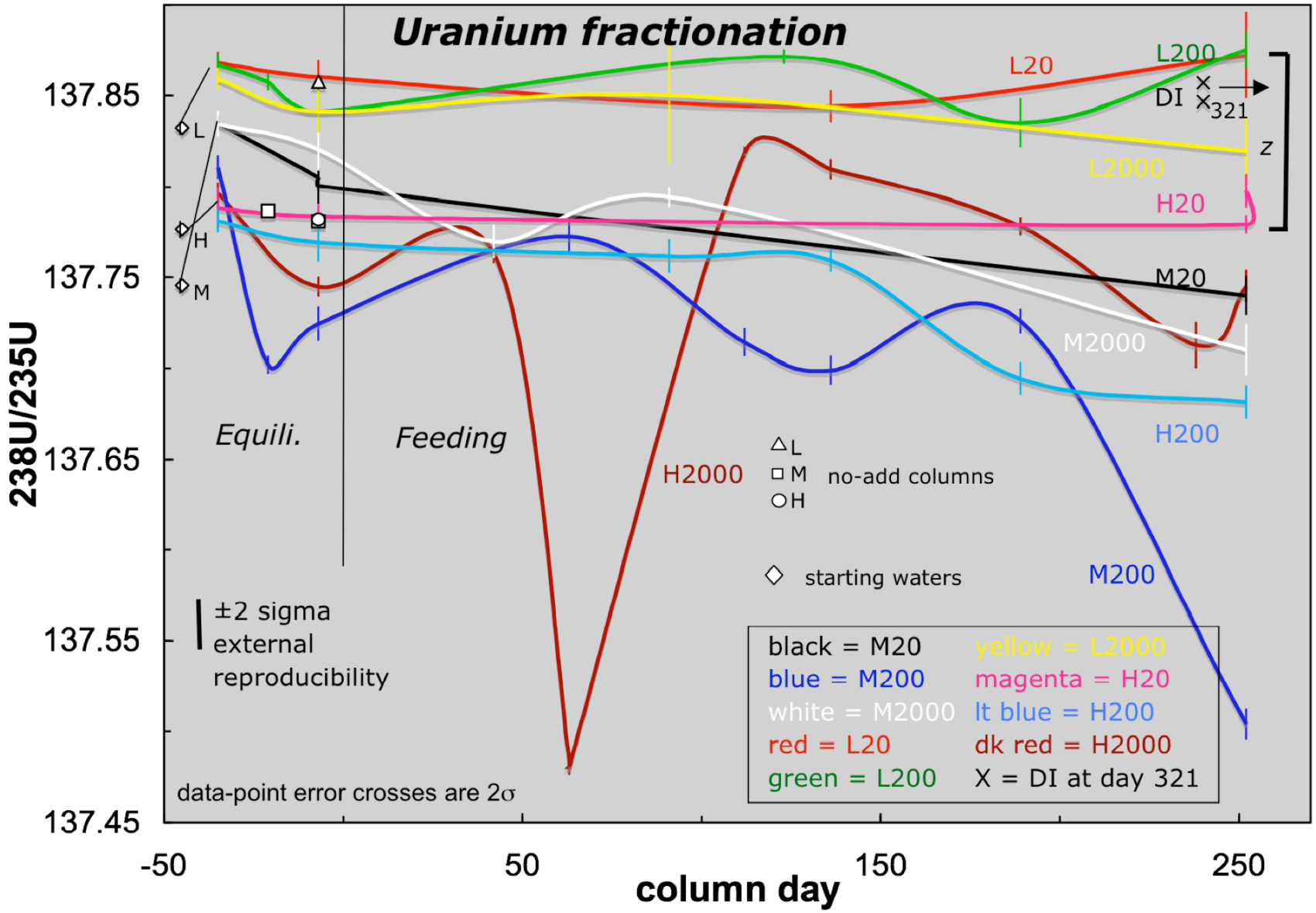
Uranium/Carbonate Concentrations



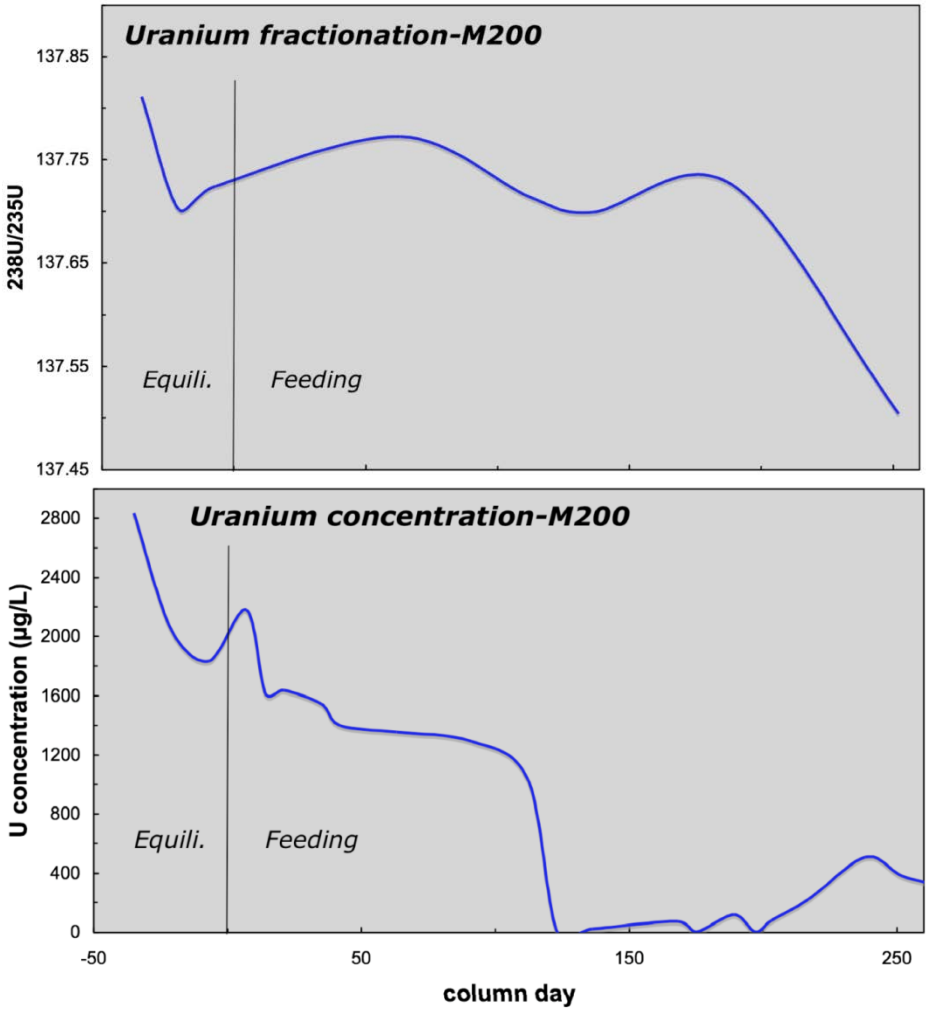


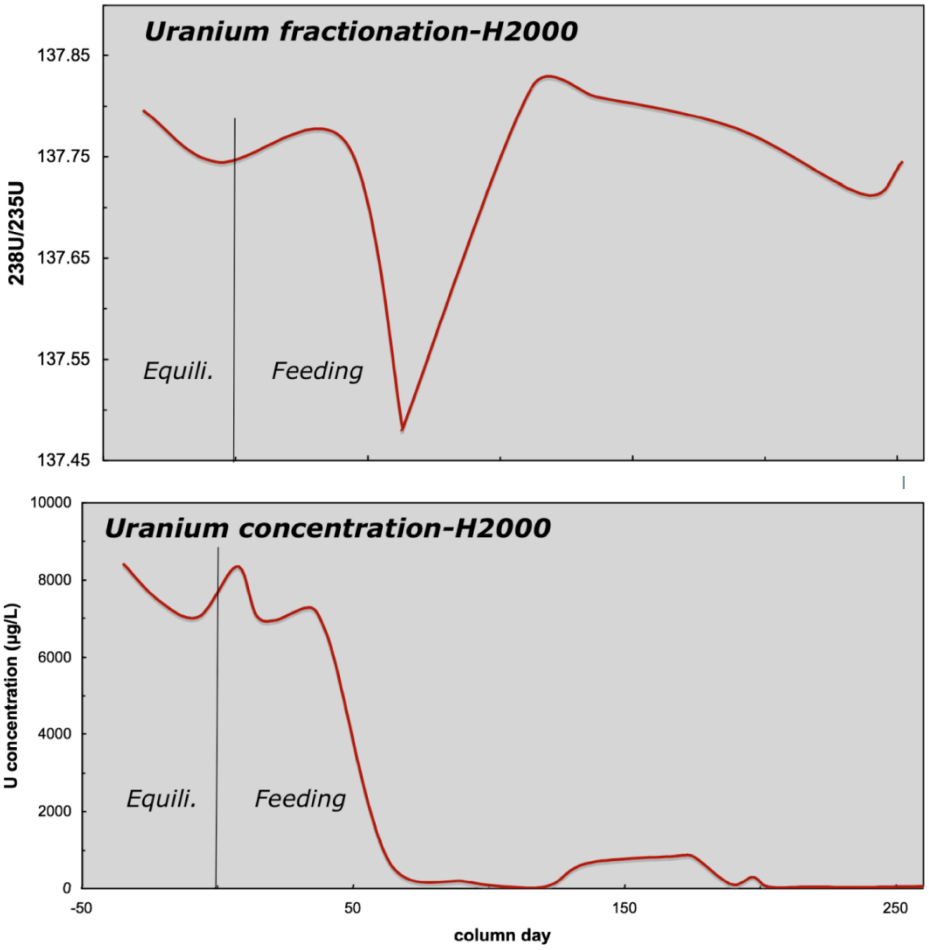





Uranium fractionation
238U/235U
137.85
137.75
137.65
137.55
137.45
-50
50
150
250
column day
L20
L200
DI
X
321
z
L2000
H20
M20
M2000
H200
M200
H2000
L
H
M
Equili.
Feeding
△L
□M
○H
no-add columns
◇ starting waters
±2 sigma
external
reproducibility
data-point error crosses are 2σ
black = M20
blue = M200
white = M2000
red = L20
green = L200
yellow = L2000
magenta = H20
lt blue = H200
dk red = H2000
X = DI at day 321

Uranium Fractionation/Concentrations





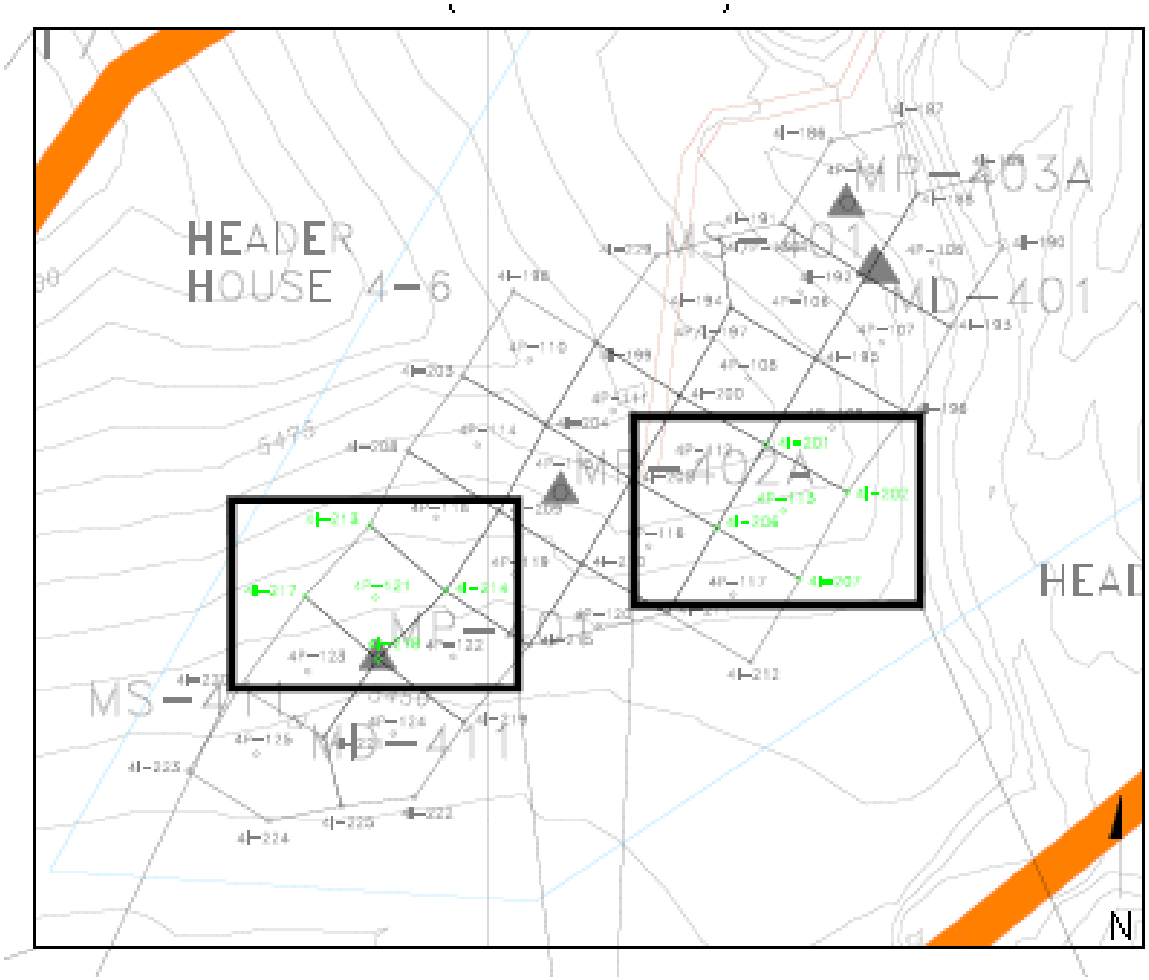
Conclusions of Column Study

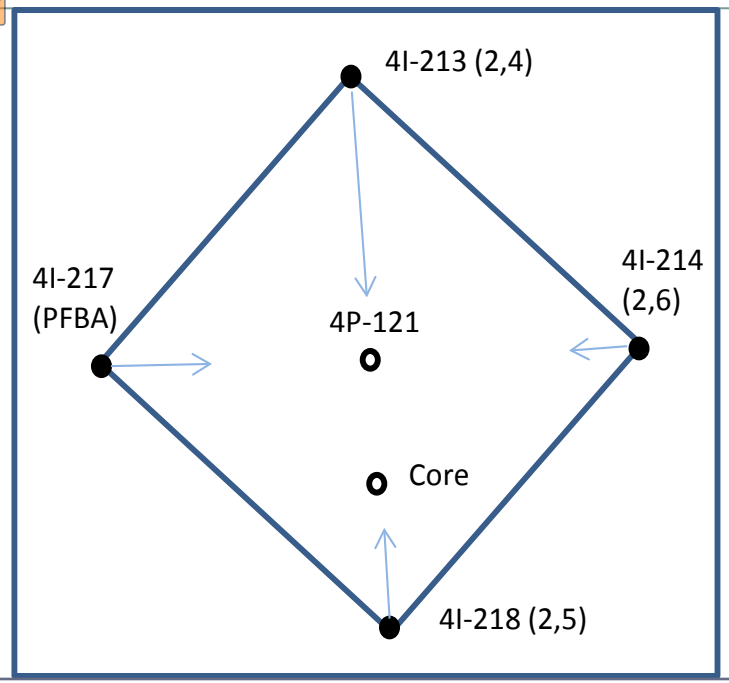
- Tryptone was effective at promoting microbial growth and reduction of uranium in a continuous flow system
  - Clogging due to stimulation not observed
  - 2ooo mg/L of tryptone shown effective at 7-8 mg/L uranium
  - 200 mg/L of tryptone shown effective at 2-3 mg/L uranium
  - 20 mg/L did not display reduction different from No Add control
- Monitoring metrics:
  - Carbonate concentration syncs well with uranium reduction activity
  - Uranium isotopic fractionations syncs well with uranium reduction activity
    - $^{238}U/^{235}U$ fractionation very sensitive to changes in U concentration, including increases

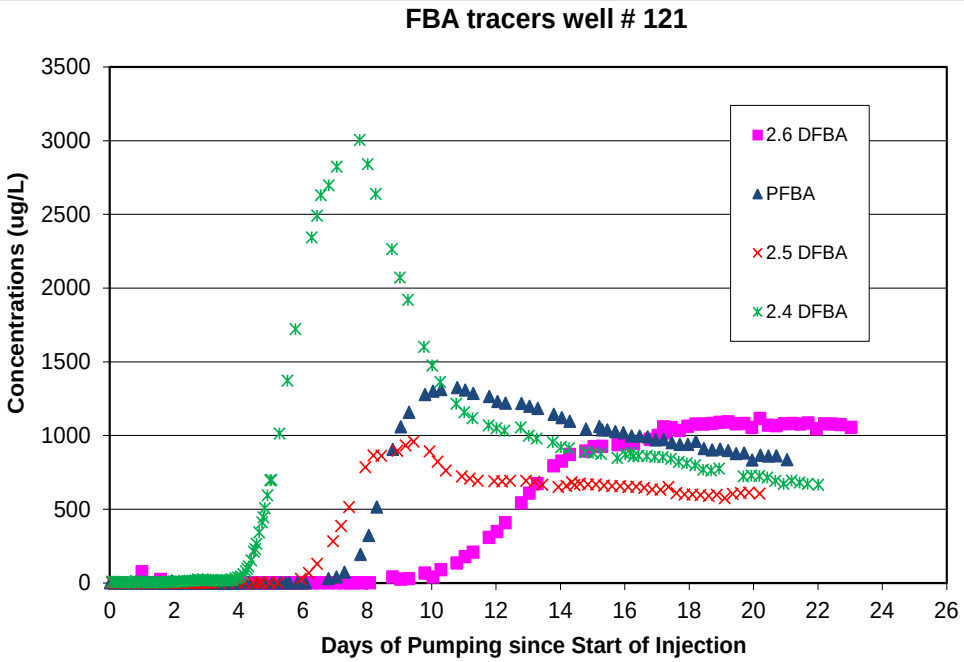
Field Trial Experiment Objectives

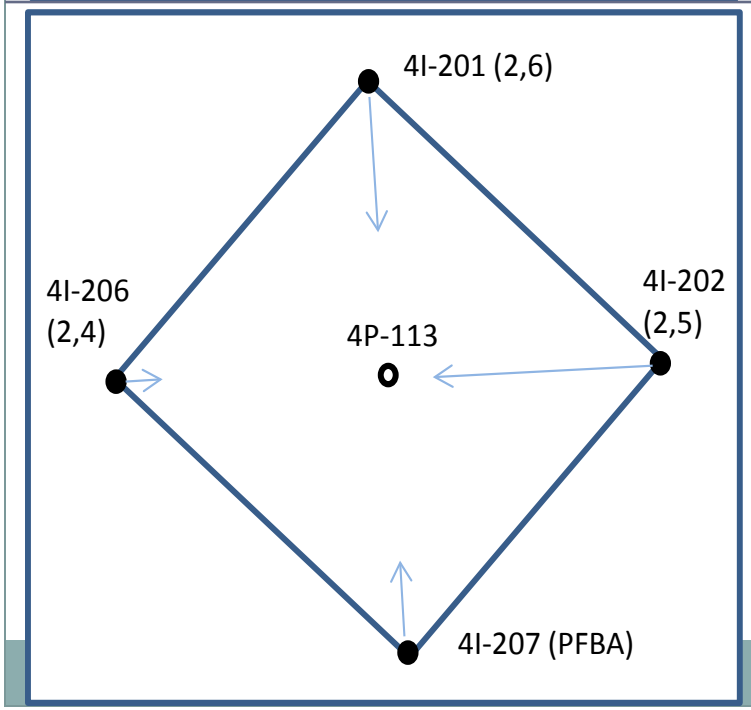
- Evaluate tryptone for its ability to promote biological reduction of Uranium (VI) in a field situation
- Continue monitoring metrics to determine effective measurements to demonstrate biological reducing situations
  - Water chemistry analyses
  - Carbon-isotopic/carbonate analyses
  - Uranium-isotopic analyses
  - Microbial community analyses
- Demonstrate biostimulation practicality
  - To ease some regulatory questions from previous efforts

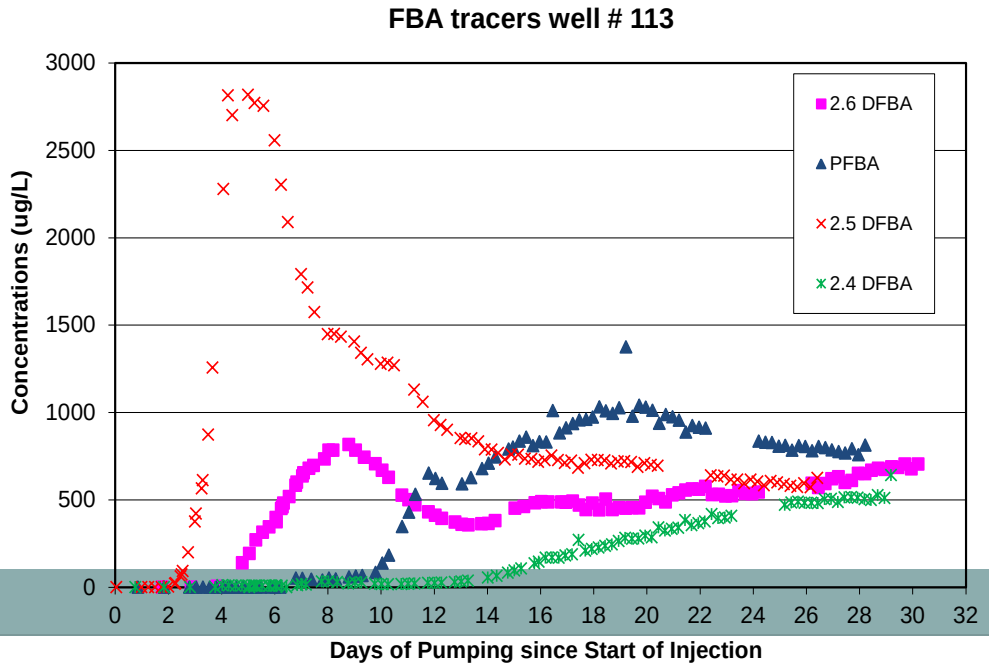
Field test for bio-stimulation




4I-213 (2,4)
4I-217
(PFBA)
4I-214
(2,6)
4P-121
Core
4I-218 (2,5)

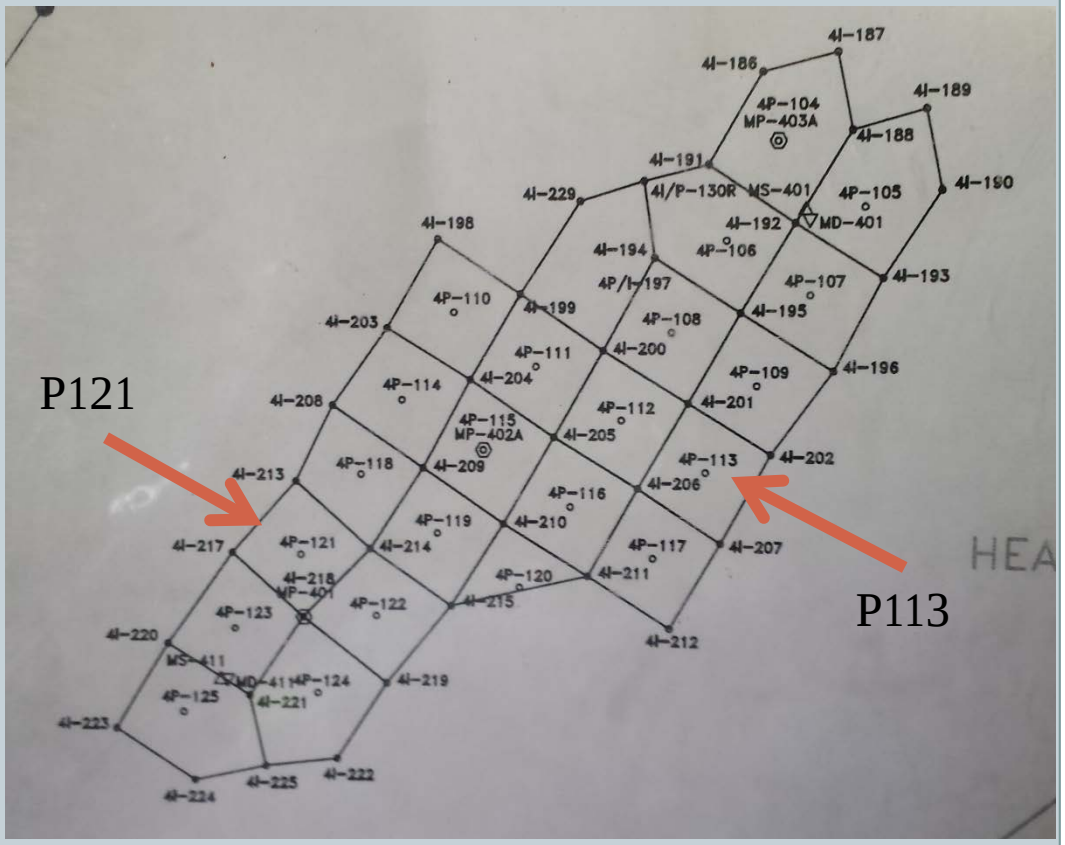

FBA tracers well # 121
Concentrations (ug/L)
Days of Pumping since Start of Injection
2.6 DFBA
PFBA
2.5 DFBA
2.4 DFBA


4I-201 (2,6)
4I-206
(2,4)
4I-202
(2,5)
4P-113
4I-207 (PFBA)

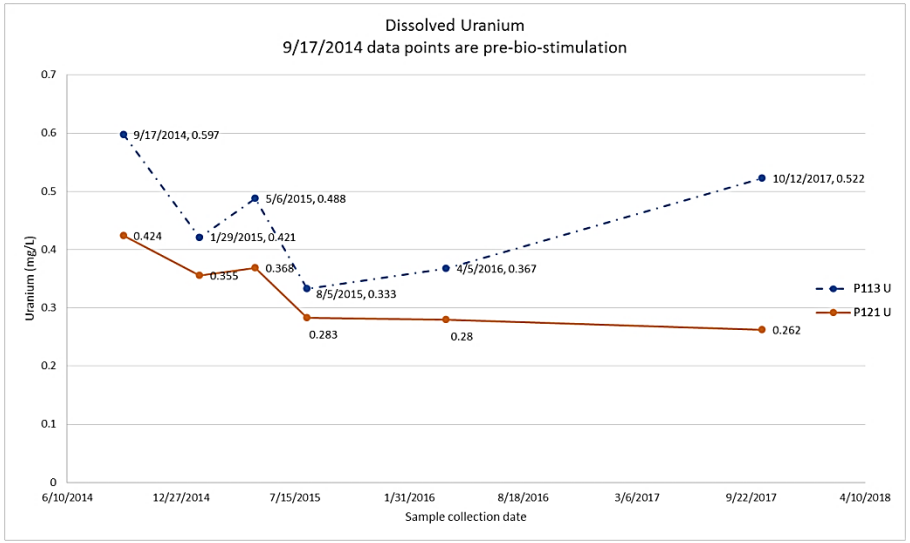

FBA tracers well # 113
Concentrations (ug/L)
Days of Pumping since Start of Injection
2.6 DFBA
PFBA
2.5 DFBA
2.4 DFBA

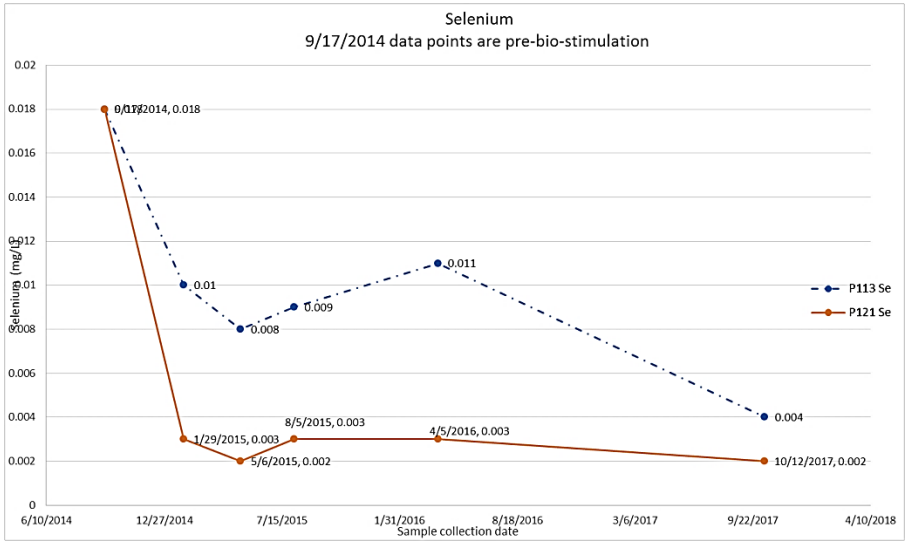
Field Trial at SRH

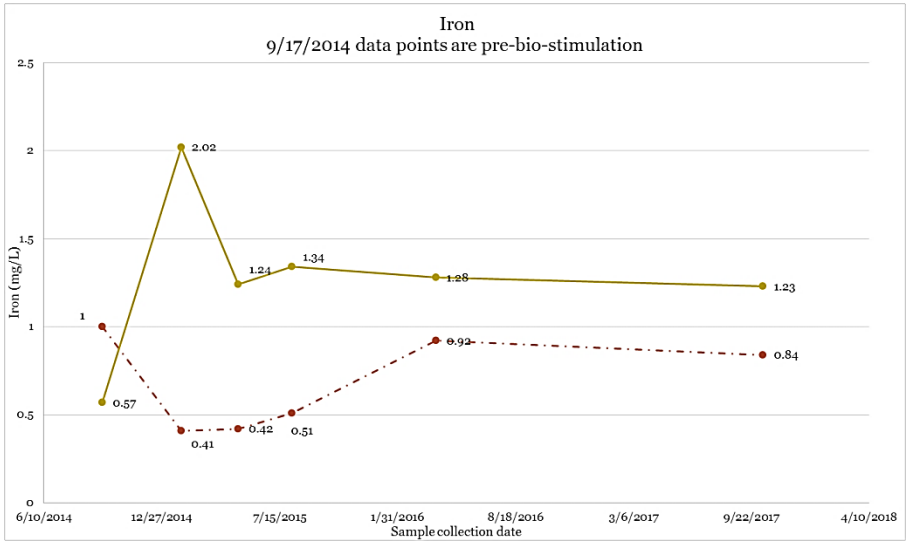
- Tryptone stimulation with longer-term monitoring in one field pattern in Mine Unit 4 at SRH
  - Stimulated P121 well pattern with tryptone (~80 mg/L)
    - 200kg total
  - Well pattern P113 used as control pattern
- Tryptone added Sept-Oct 2014

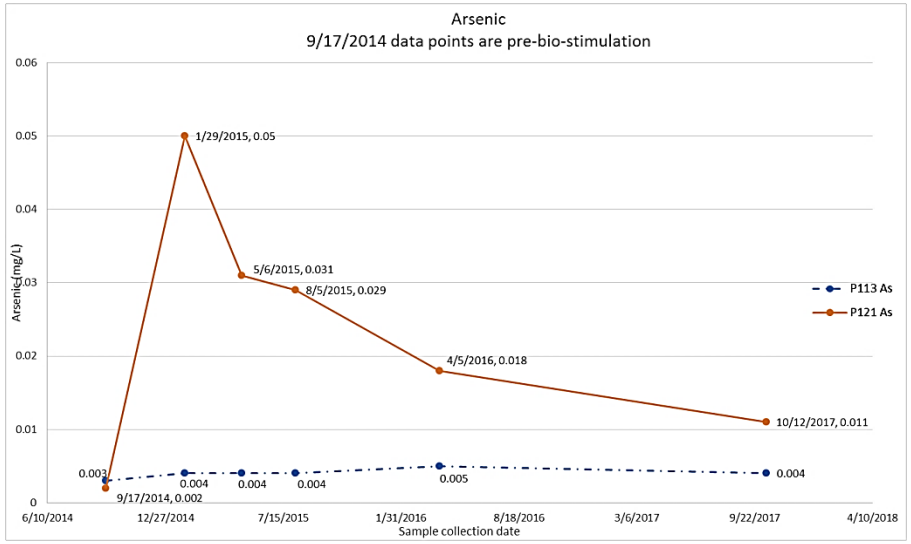


Measured Concentrations

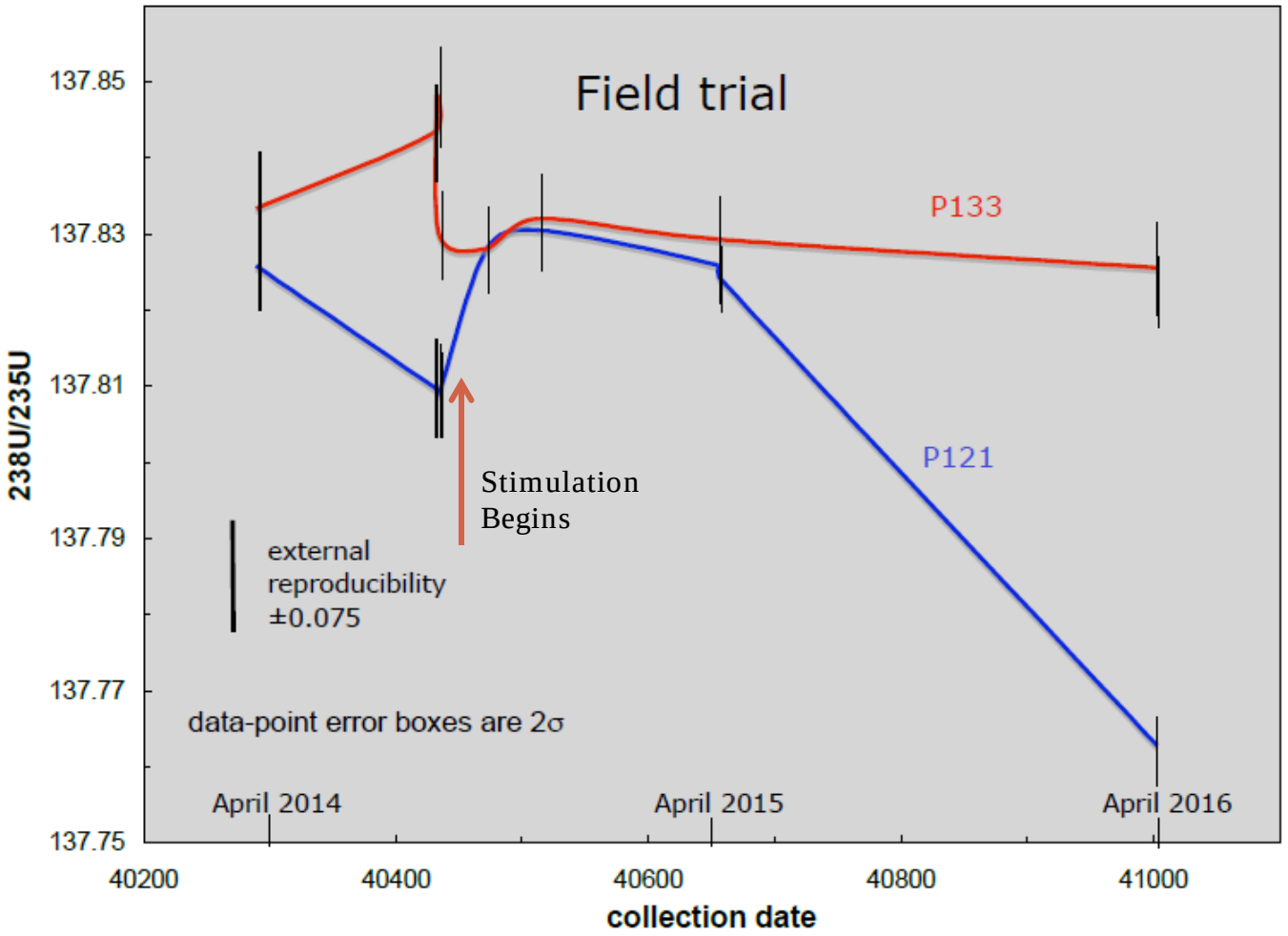








Uranium Fractionation



Conclusions of Field Trial

- Reducing environment:
  - Overall, data suggest a reducing environment in stimulated well pattern P121
    - Selenium & uranium concentrations decrease
    - Arsenic & iron (ferrous) concentrations increase
  - Uranium isotopic fractionation is significant in stimulated environment
- Most recent data may suggest increased stability of reduced uranium in the stimulated pattern
  - More data necessary

Field Trial Thoughts, Future Directions

- Tryptone quantity added was likely too low
  - Only ~40% of the low value suggested based upon column data
- Was this the proper point in restoration to bioremediate?
  - Didn't clog any wells
  - In-lab studies show reduction at higher levels, plus bottom level in microcosms was close to 0.4ppm
- What makes tryptone effective?
  - Carry-on lab trial is providing insight

Acknowledgements

- Cameco, Inc.
- State of Wyoming Legislature, ISRU Technology Research Program
  - UW School of Energy Resources

Cameco

Cameco Resources

School of Energy Resources