Sustainable In-situ Remediation Approach for Arsenic Impacted Groundwater

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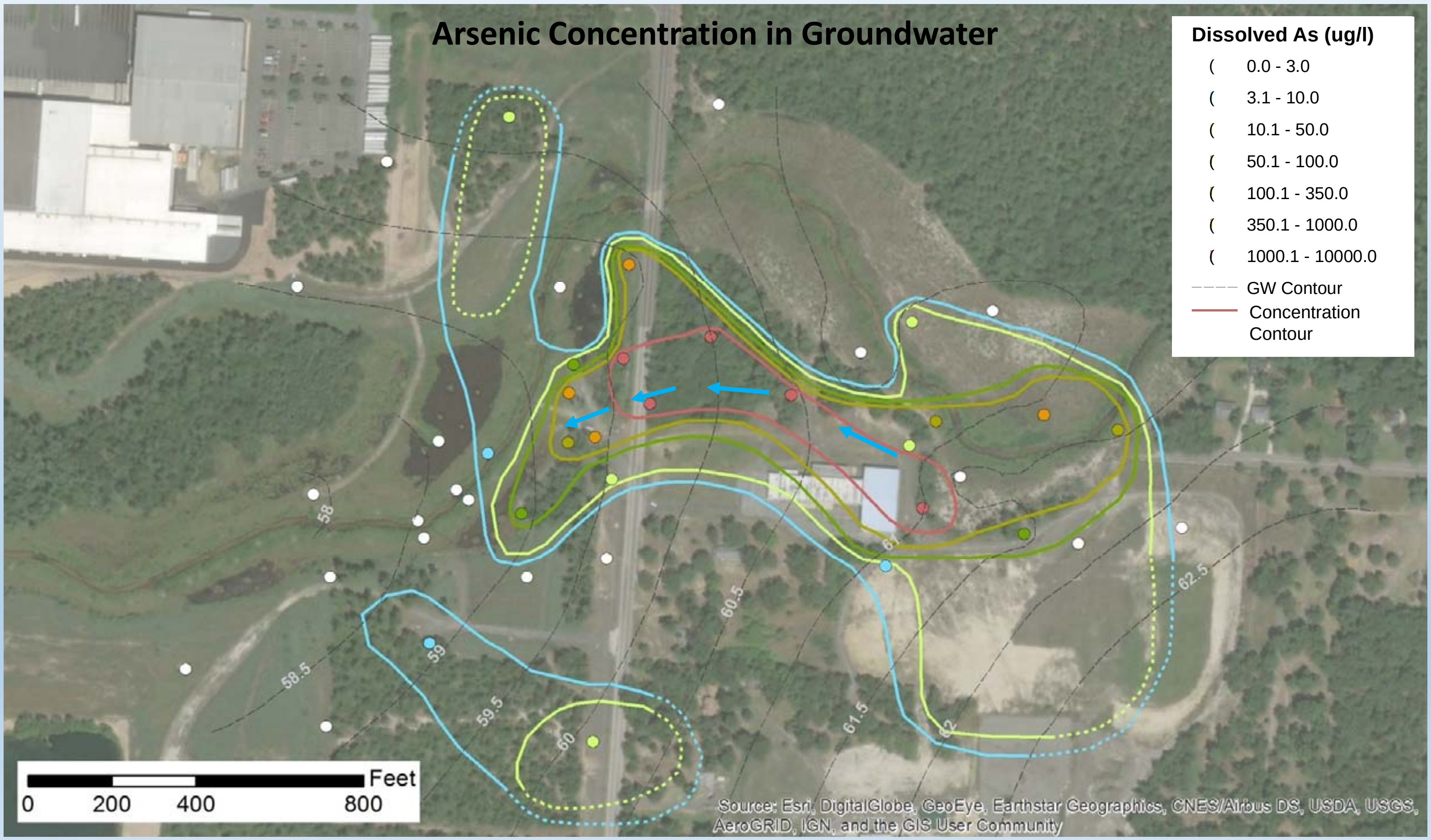
Site background

Vineland Chemical Company Superfund Site, Vineland, NJ



In-situ Immobilization of Arsenic

Air Sparging

Soil and Groundwater Characterization

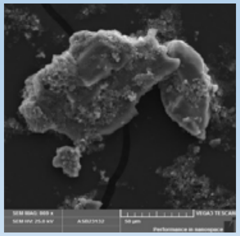
Ambient Conditions

Groundwater

- Anoxic
  - D.O. < < 1 mg/l
  - ORP ≈ -100mV - +50mV
- Dissolved arsenic > 1 mg/L
  - As (III) dominant over As (V)
- Dissolved iron ≈ 15-20 mg/L
- pH ≈ 4.5-6

Soil

- Iron minerals in soil: goethite, hematite
  - Other minerals: quartz, kaolinite
- High arsenic concentrations coincide with high iron concentrations
- Arsenic (III) sorbs to iron oxides

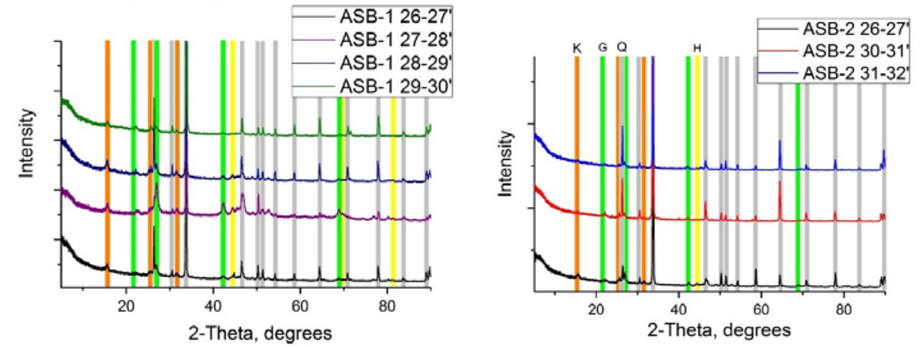


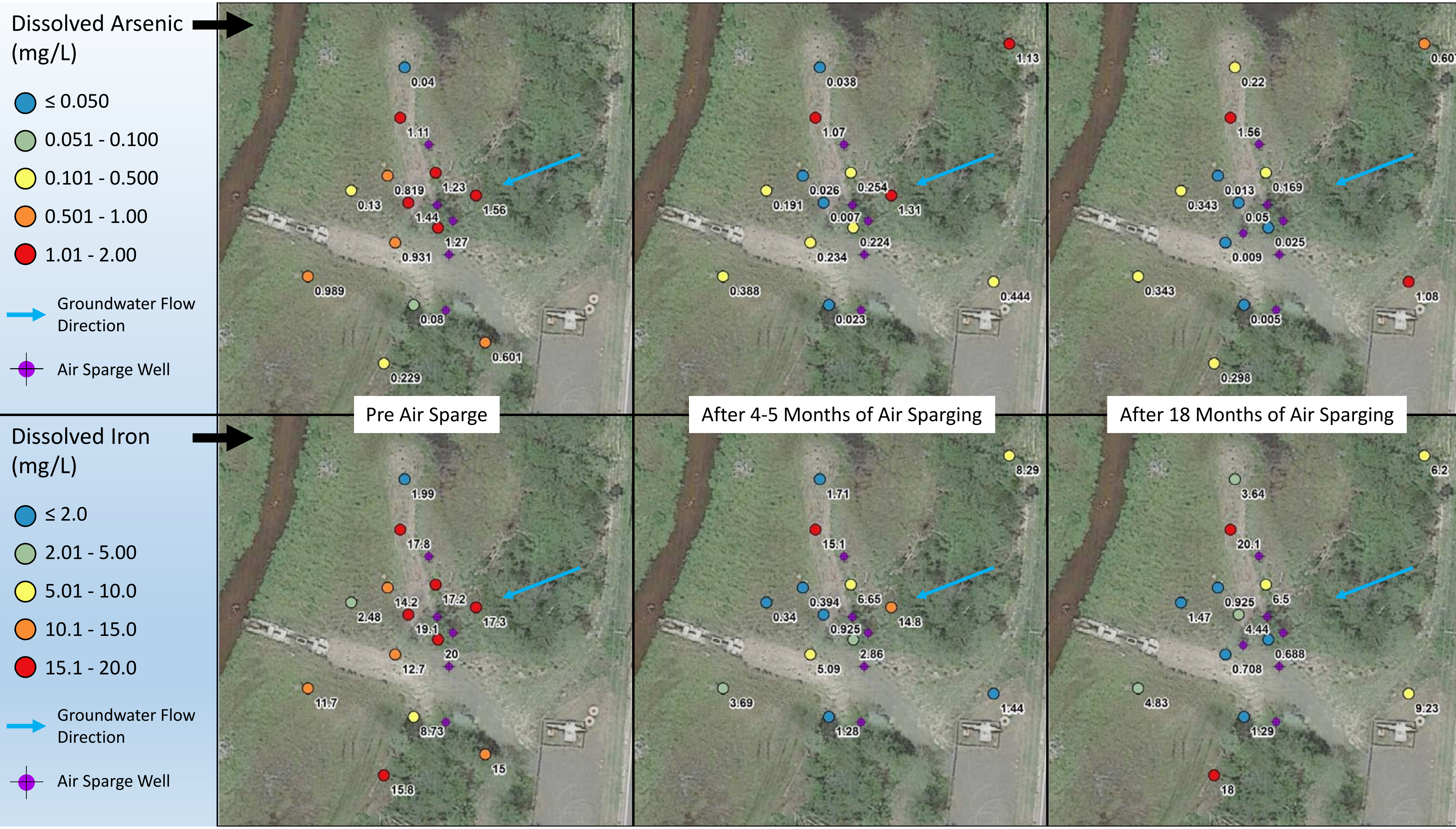
Air Sparge Conditions

Groundwater

- Aerobic
  - D.O. → solubility (>10 mg/L)
  - ORP: increased to > 300 mV
- Dissolved arsenic reduced to < 0.01 mg/L
  - As (III) dominant over As (V)
- Dissolved iron reduced to as low as 0.01 mg/L
- pH: stable to slight increase

XRD Results





Dissolved Arsenic (mg/L)
≤ 0.050
0.051 - 0.100
0.101 - 0.500
0.501 - 1.00
1.01 - 2.00
Groundwater Flow Direction
Air Sparge Well
0.04
1.11
0.819
1.23
0.13
1.56
1.44
1.27
0.931
0.989
0.08
0.601
0.229
1.13
0.038
1.07
0.026
0.254
0.191
1.31
0.007
0.224
0.234
0.388
0.444
0.023
0.607
0.22
1.56
0.013
0.169
0.343
0.05
0.025
0.009
0.343
1.08
0.005
0.298
Pre Air Sparge
After 4-5 Months of Air Sparging
After 18 Months of Air Sparging
Dissolved Iron (mg/L)
≤ 2.0
2.01 - 5.00
5.01 - 10.0
10.1 - 15.0
15.1 - 20.0
Groundwater Flow Direction
Air Sparge Well
1.99
17.8
14.2
17.2
2.48
17.3
19.1
20
12.7
11.7
8.73
15
15.8
8.29
1.71
15.1
0.394
6.65
0.34
14.8
0.925
2.86
5.09
3.69
1.44
1.28
6.2
3.64
20.1
0.925
6.5
1.47
4.44
0.688
0.708
4.83
9.23
1.29
18

Study Goals

- Identify processes responsible for in-situ immobilization of arsenic by air sparging
- Identify optimal conditions for arsenic immobilization
- Develop a numerical tool that can predict arsenic removal under field conditions

Approach

- Laboratory sorption tests using site soil and groundwater
  - Monitor As/Fe changes in batch/column tests
- Geochemical modeling with calibration to laboratory data
- Model verification to field data under anaerobic and air sparge conditions

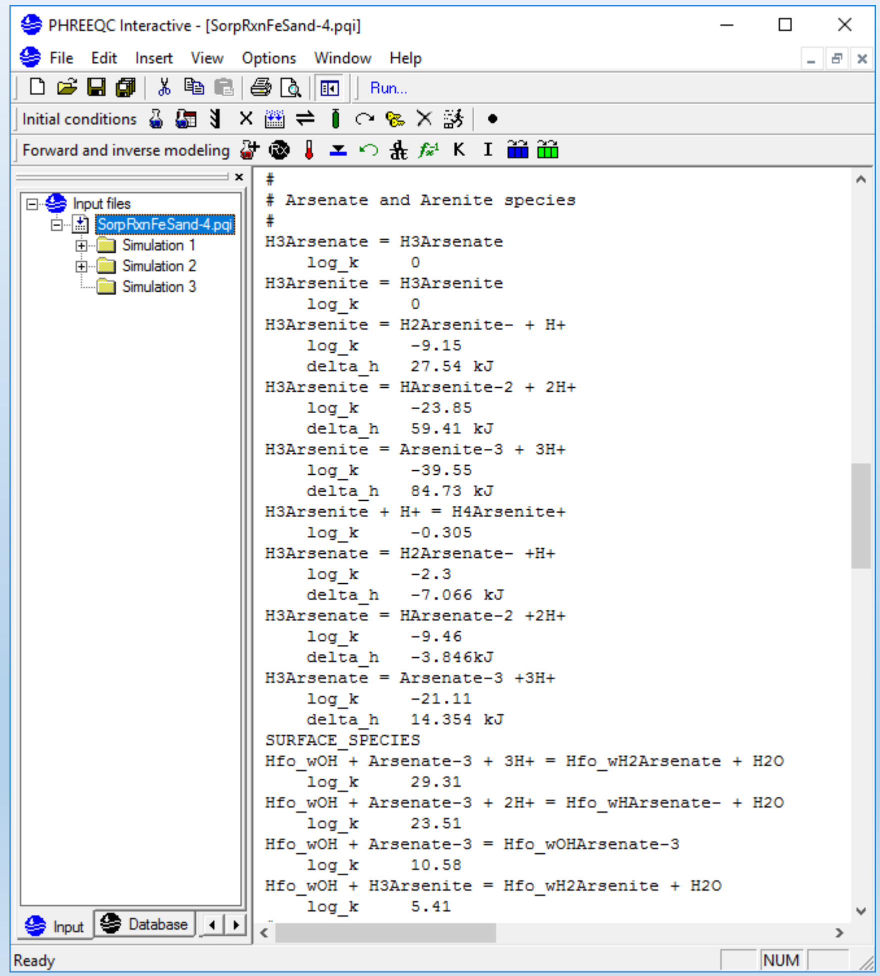
Geochemical Modeling Approach

- PHREEQC version 3 and wateq4f data base
- Sorption of arsenic to iron oxides
  - Hydrous ferric oxide (HFO) surface complexation model from Dzombak and Morel (1990)
    - Specific Surface Area = 600 m^2/g
    - Weak site density = 0.2 moles per mole of iron
    - Mass set by decrease in dissolved Fe plus small percentage of Fe in soil
- Kinetic oxidation of Fe (II) to Fe (III)

$$rate = -k_{hom}[Fe(II)][O_2][H^+]^{-2} - k_{het}[Fe(III)][Fe(II)][O_2][H^+]^{-1}$$

k_{hom}=8.4E-14 mol/L/sec*
k_{het}=9.5E-04 L/mol/sec*

- Degassing of CO_2
- NOT modeling As (III) oxidation to As (V)
  - Kinetics are slow under ambient conditions



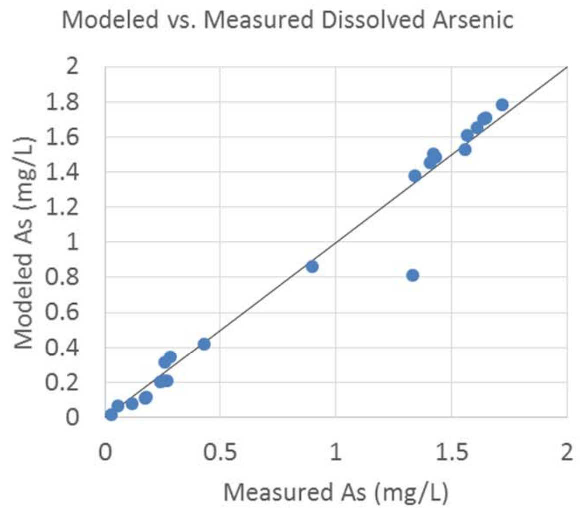
*Dietz, J. M., and Dempsey, B. A., 2001. Treatment of Mine Drainage Using Recirculated Iron Oxides In: A Complete Mix Reactor. Proceedings of the 2001 National Association of Abandoned Mine Lands Annual Conference, August 19-22, 2001, Athens, Ohio

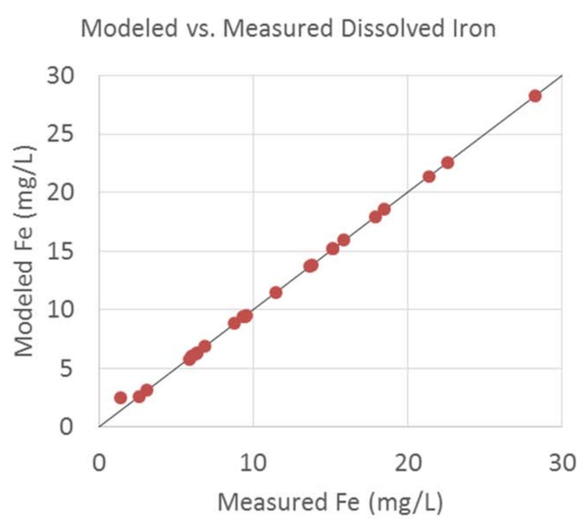
Model Calibration Results

<u>Assumptions:</u>

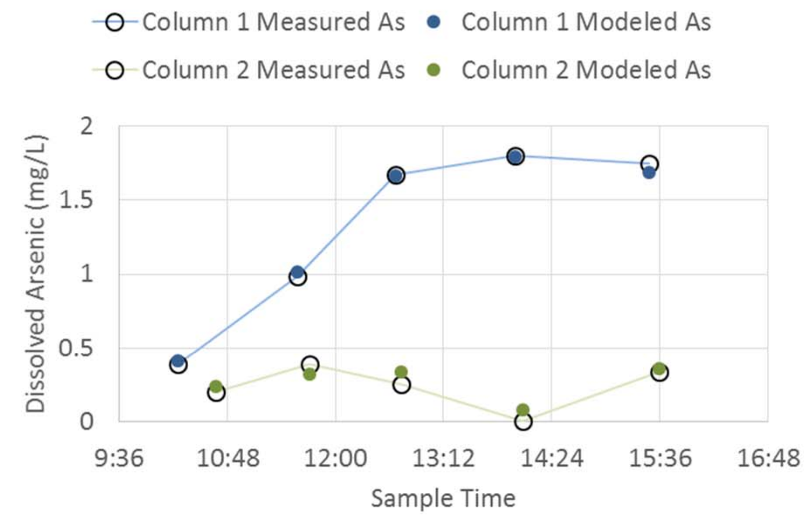
1. Mass of freshly precipitated Fe modeled as HFO sorption surface
2. 2% - 5% Fe in soil modeled as sorption surface (batch tests)
   - Less for column tests (< 0.1%)
3. D.O. = 0.2 mg/l - 0.8 mg/l
4. CO_2 degassing: 10% - 60% of initial concentration

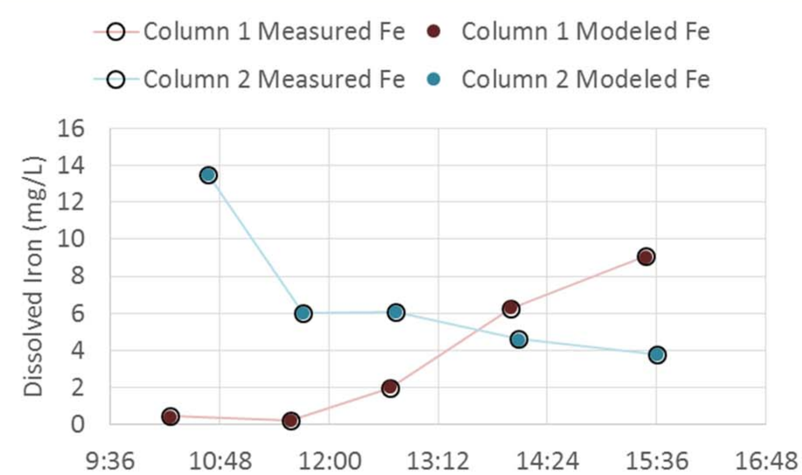
Batch Test Results





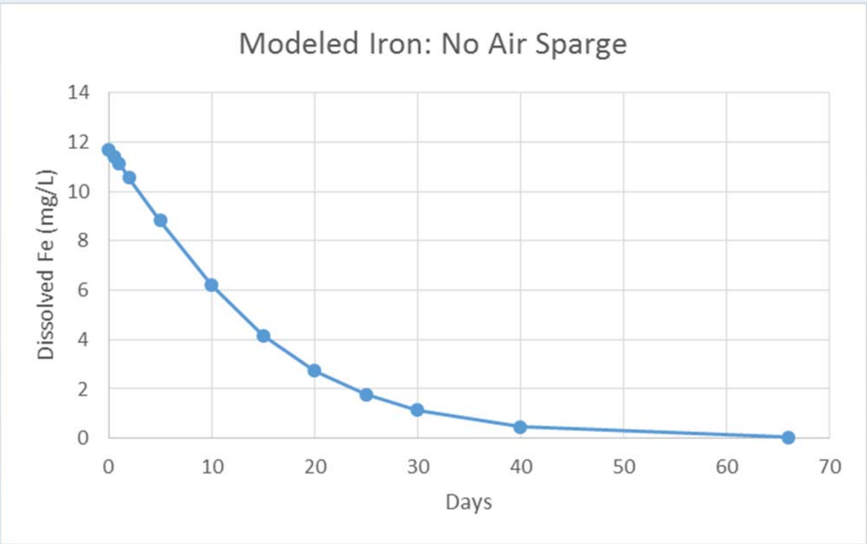
Column Test Results





Column 1 = Low Fe Sand
Column 2 = High Fe Sand

Model Application to Field: Ambient Conditions

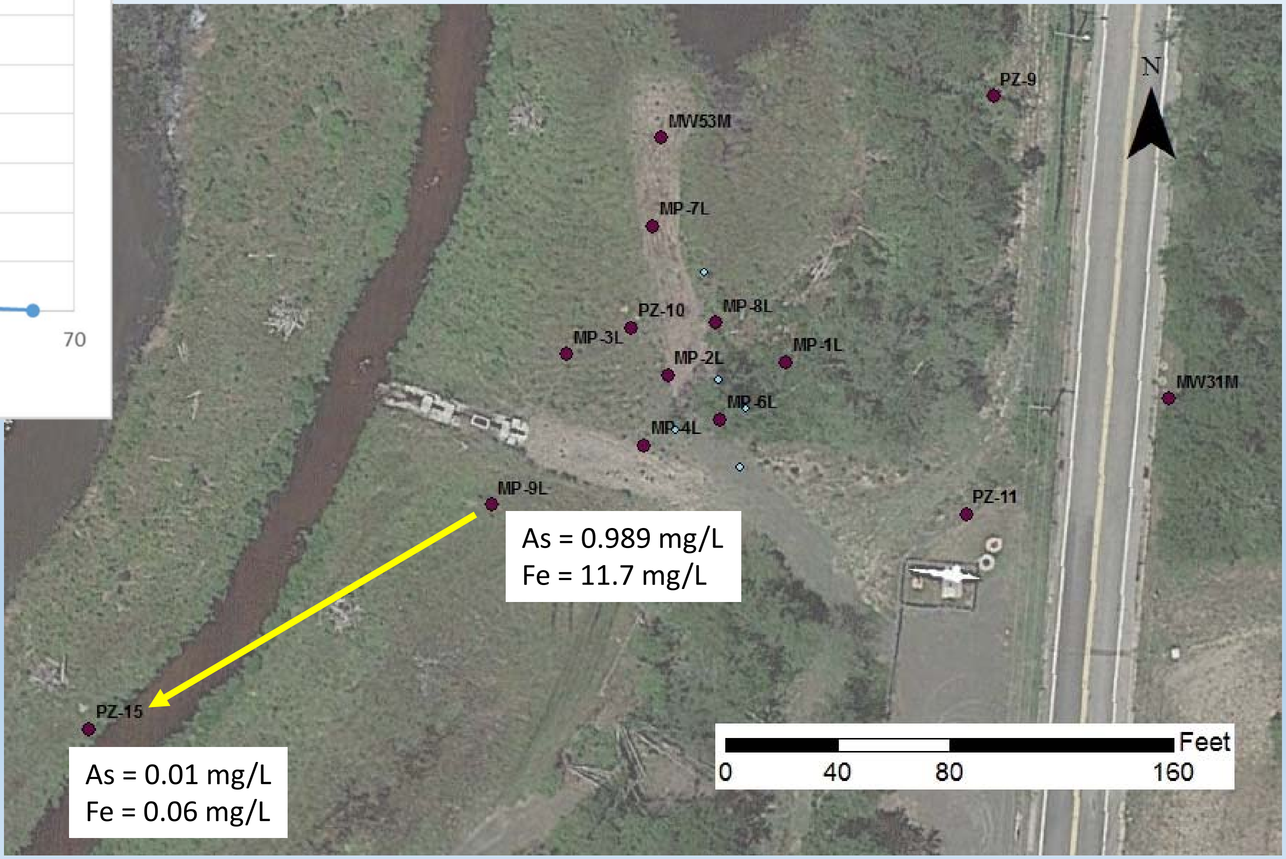


Groundwater flow between MP-9L and PZ-15

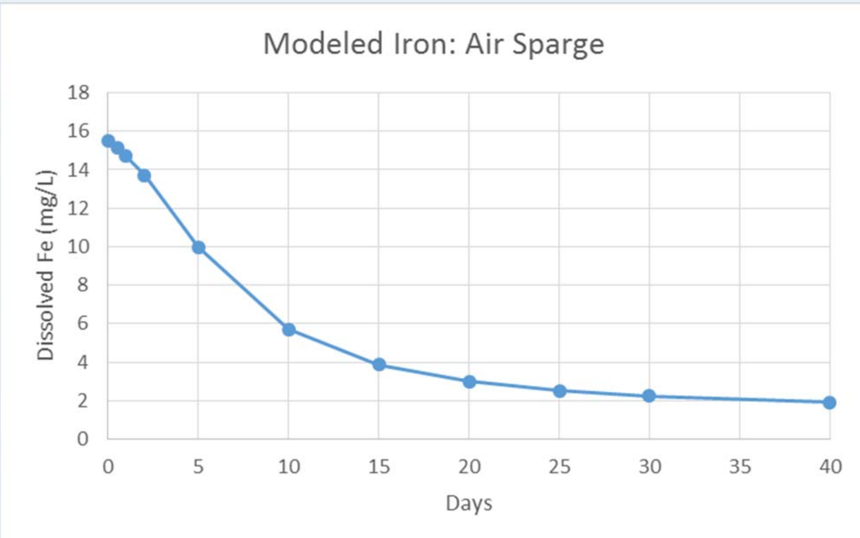
Distance = 165 ft
Average Groundwater Flow Velocity = 2.5 ft/day
Travel Time = 66 days

pH = 5.8
D.O. = 0.1 mg/L
All precipitated Fe + 1% Fe in soil = HFO sorption surface

Model Calculated Fe @ PZ-15 = 0.044 mg/L
Model Calculated As @ PZ-15 = 0.02 mg/L



Model Application to Field: Air Sparging

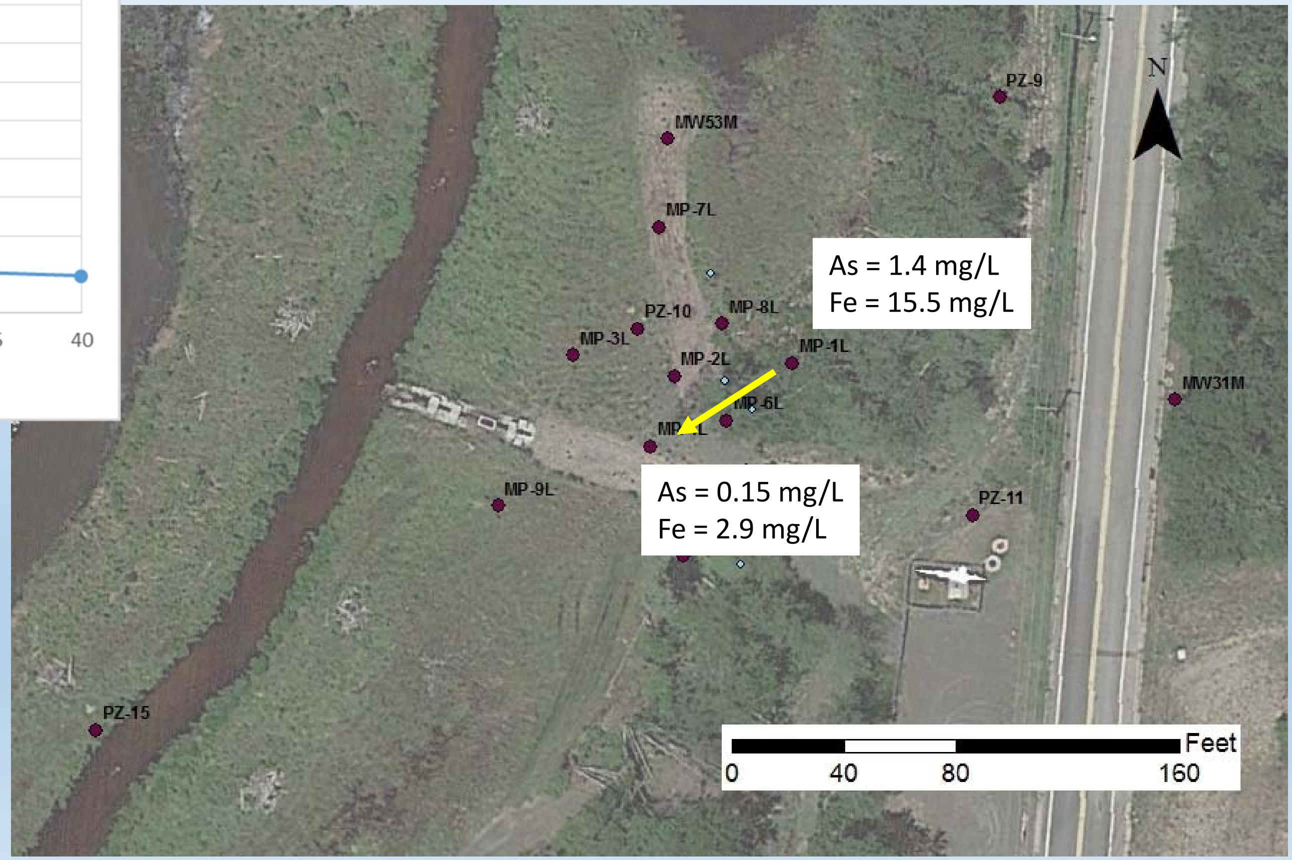


Groundwater flow between MP-1L and MP-4L

Distance = 50 ft
Average Groundwater Flow Velocity = 2.5 ft/day
Travel Time = 20 days

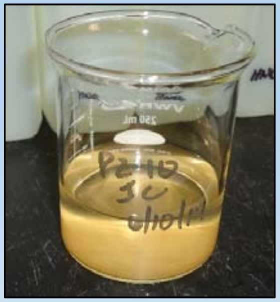
pH = 5.5
D.O. = 2.0 mg/L
All precipitated Fe + 1% Fe in soil = HFO sorption surface

Model Calculated Fe @ MP-4L = 3.0 mg/L
Model Calculated As @ MP-4L = 0.14 mg/L



Findings

- Arsenic sorbs to freshly precipitated iron
  - Accounts for approx. 80% of arsenic sorption with remaining arsenic sorbing to Fe oxides in the soil
  - As (III) does not have to oxidize to As (V) to sorb
- Iron oxidation controlled by pH & D.O.
  - Optimal operating conditions -> NOT instantaneous precipitation
- pH controlled by iron chemistry and CO_2 degassing



Next steps

- Refine performance measures for air sparge system
  - pH/D.O./ORP
- Full scale air sparge design
- Stabilization testing