

*Presentation for:*

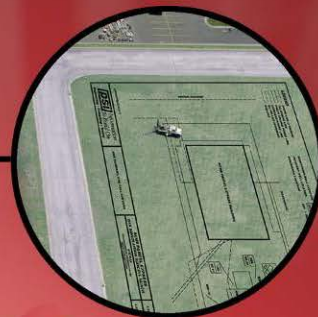
**FDEP  
BUREAU OF WASTE SITE  
CLEANUP SECTION  
CONTRACTOR WORKSHOP**

**CASE STUDY: BIOGEOCHEMICAL  
REDUCTIVE DEHALOGENATION  
(BIRD) PILOT STUDY**

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**MAY 2016**

Site Selection  
Support Services



Design  
Support Services



Construction  
Support Services



Property Management  
Support Services



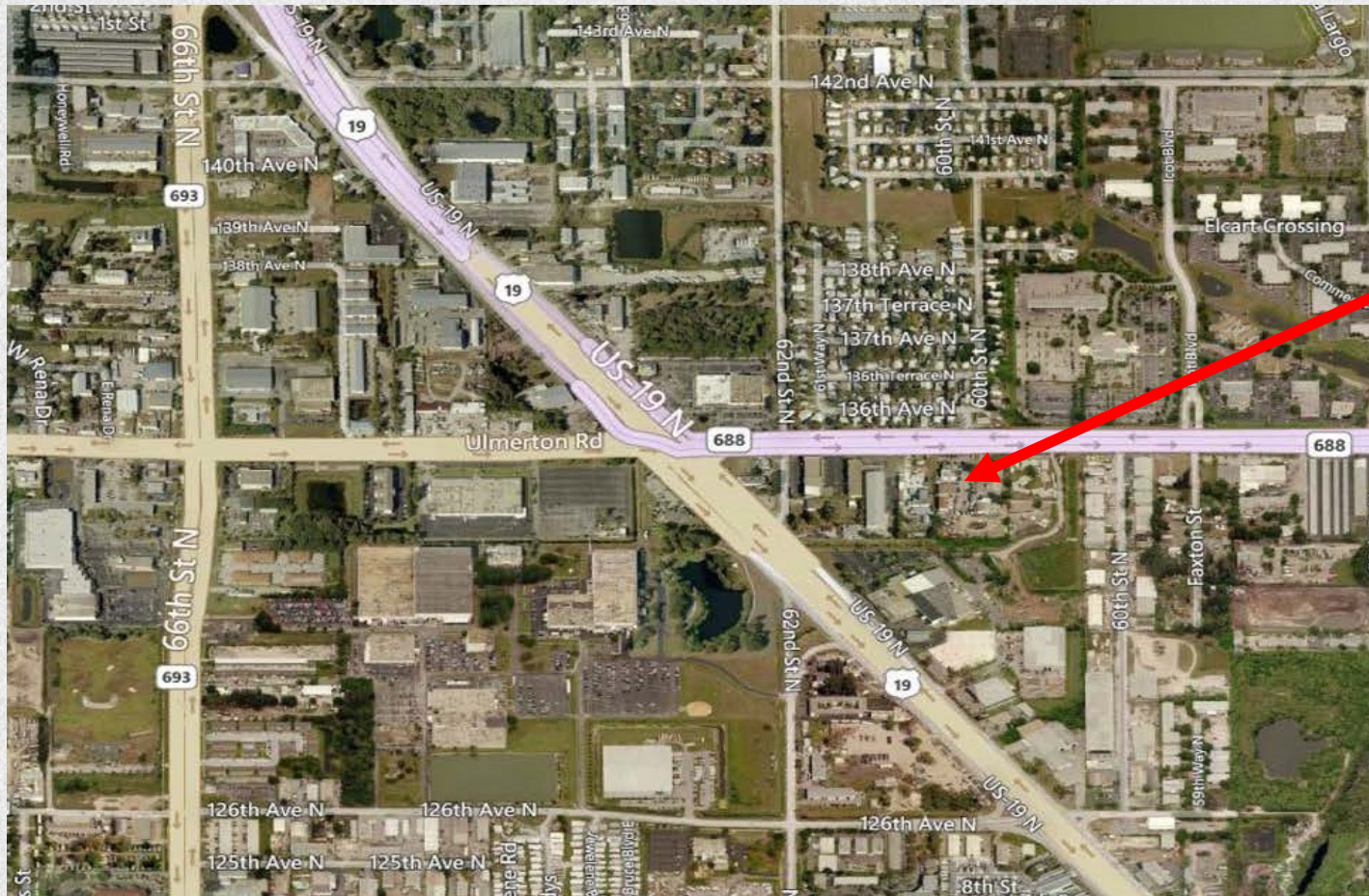
# Discussion Outline

- Site Background
- Site Assessment
- BiRD Pilot Test
- Results
- Conclusion



# Site Location

- Central Pinellas County, industrial area



# Site Background

- Property owned by Huss Family
- Property leased to National Foundation Services – asphalt & construction testing firm
- Asphalt testing since ~1963
- Tenant business bought by PSI
- Property use has been light industrial
- Current Owner – Knight Enterprises, cable installation company

# Site Location



**Source  
area**



**LEGEND**

- SHALLOW MONITOR WELL LOCATION
- INTERMEDIATE MONITOR WELL LOCATION
- DEEP MONITOR WELL LOCATION
- INJECTION WELL LOCATION
- CLUSTER WELL LOCATION
- VAPOR MONITORING WELL LOCATION
- APPROXIMATE SUBJECT PROPERTY BOUNDARY

REFERENCE: THE 2014 AERIAL PHOTOGRAPH WAS OBTAINED FROM FOOT

0 30 60 120 Feet

1 inch = 60 feet

# Site Background



- Asphalt Testing Laboratory – Used 1,1,1-TCA and TCE in the 1970's.
- Asphalt testing procedures.
- Submerge Hot Mix Asphalt sample in a solvent to disintegrate the sample.
- Centrifuge to separate.
- Waste solvent stored behind building with apparent discharge of unknown quantity.



# Site Background

- During property transfer due diligence, environmental assessment revealed 1000 ug/L of 1,1,1-TCA
- Initiated comprehensive site assessment

| Monitor Well | 1,1,1-TCA<br>ug/L | 1,1-DCA<br>ug/L | 1,1-DCE<br>ug/L | Chloro<br>ethane<br>ug/L | Vinyl<br>chloride<br>ug/L |
|--------------|-------------------|-----------------|-----------------|--------------------------|---------------------------|
| GCTL         | 200               | 70              | 7               | 12                       | 1                         |
| NADC         | 2000              | 700             | 70              | 1200                     | 100                       |
| Shallow      | 3,855             | 107             | 85              | <20                      | <20                       |
| Deep         | 22,830            | 24,600          | 12,400          | <50                      | 42                        |

# Site Assessment

- Shallow, intermediate, deep, deeper, deepest well installation (90 feet bls)
- Soil analytical – no shallow impact
- *Dehalococcoides* (Dhc), *vinyl chloride reductase* (vcrA), *Dehalobacter* spp. (DHBt) - incomplete pathway for dechlorination
- MAGS™ test
- Concern with migration off-site and DOT ROW during road widening



# Site Assessment

Source Area –  
underground utilities,  
aboveground utilities,  
directly adjacent to  
building, limited space  
for equipment



# Lithology

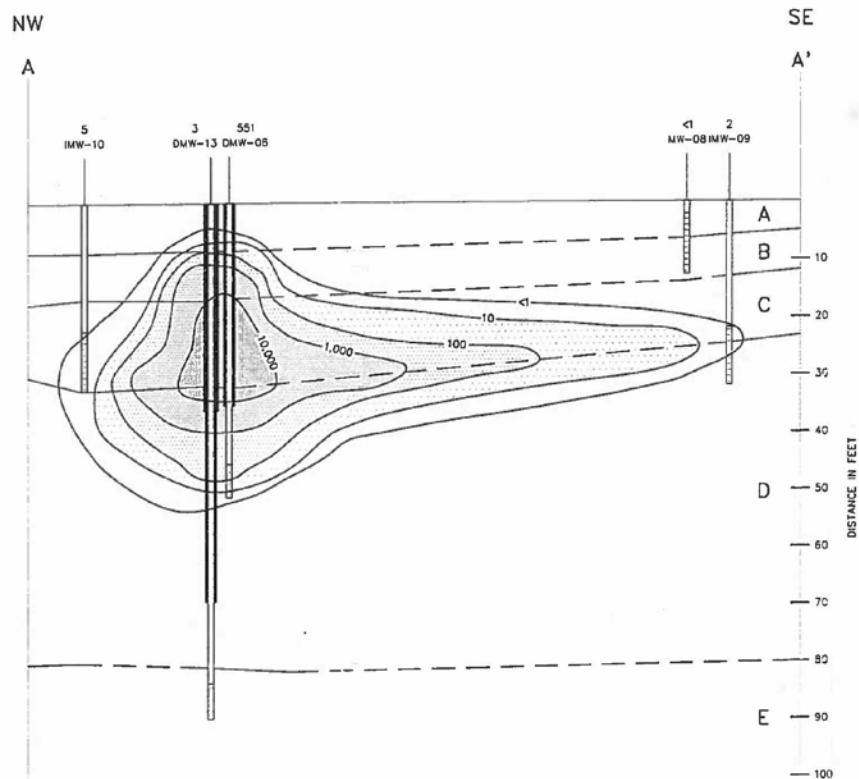
- 0 - 8 ft – silty sand
- 8 – 13 ft bls – tan to gray shelly sand
- 13 – 28 ft bls – dark brown silty sand, organics
- 28 – 35 ft bls – thin layer of sand
- > 35 ft bls- greenish gray clay  
upper Hawthorn Formation



# Site Characteristics

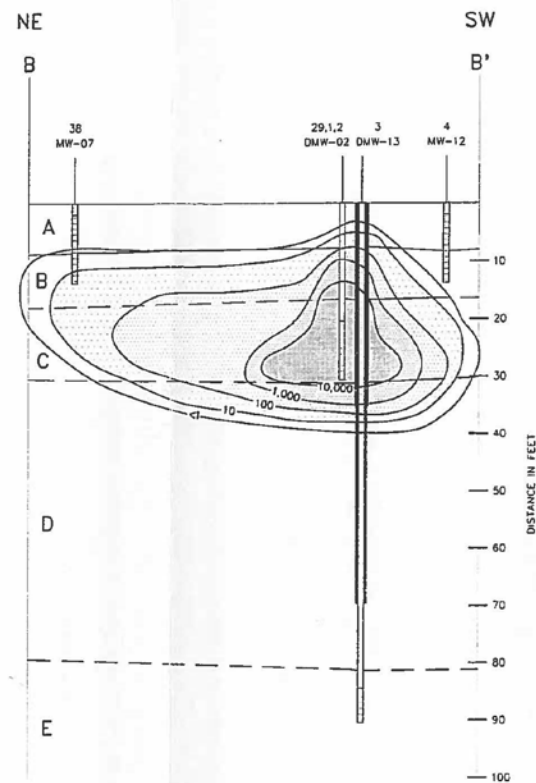
- Depth to water: Shallow 3 feet bls
- K averages 15 ft/day
- Velocity - ~39 ft/year
- Horizontal hydraulic conductivity ~10 X vertical hydraulic conductivity
- Groundwater pH - 7.0
- Reducing aquifer, low DO, Fe reducing ORP (-100 mV) , presence of 1,1-DCA, 1,1-DCE, cis-1,2-DCE, trans-1,2-DCE and vinyl chloride suggests evidence of reductive dehalogenation, and abiotic degradation

# VOH Plume



CROSS SECTION A-A'

VERTICAL SCALE: 1" = 20'  
HORIZONTAL SCALE: 1" = 50'



CROSS SECTION B-B'

VERTICAL SCALE: 1" = 20'  
HORIZONTAL SCALE: 1" = 50'

## LEGEND

- A SAND
- B SHELLY SAND
- C SILTY SAND/SILT
- D CLAY/SANDY CLAY
- E LIMESTONE

## TOTAL VOLATILE ORGANIC HALOCARBONS (VOH)

- GREATER THAN 10,000 ug/l
- GREATER THAN 1,000 ug/l
- GREATER THAN 100 ug/l
- GREATER THAN 10 ug/l

EXTENT OF DETECTABLE TOTAL VOH

1,2 DICHLOROETHANE NOT INCLUDED IN  
TOTAL VOH CONCENTRATION

**TOTAL VOH CONTOUR MAP -  
CROSS SECTIONS**  
PSI/HUSS SITE  
6056 ULMERTON ROAD  
CLEARWATER, FLORIDA

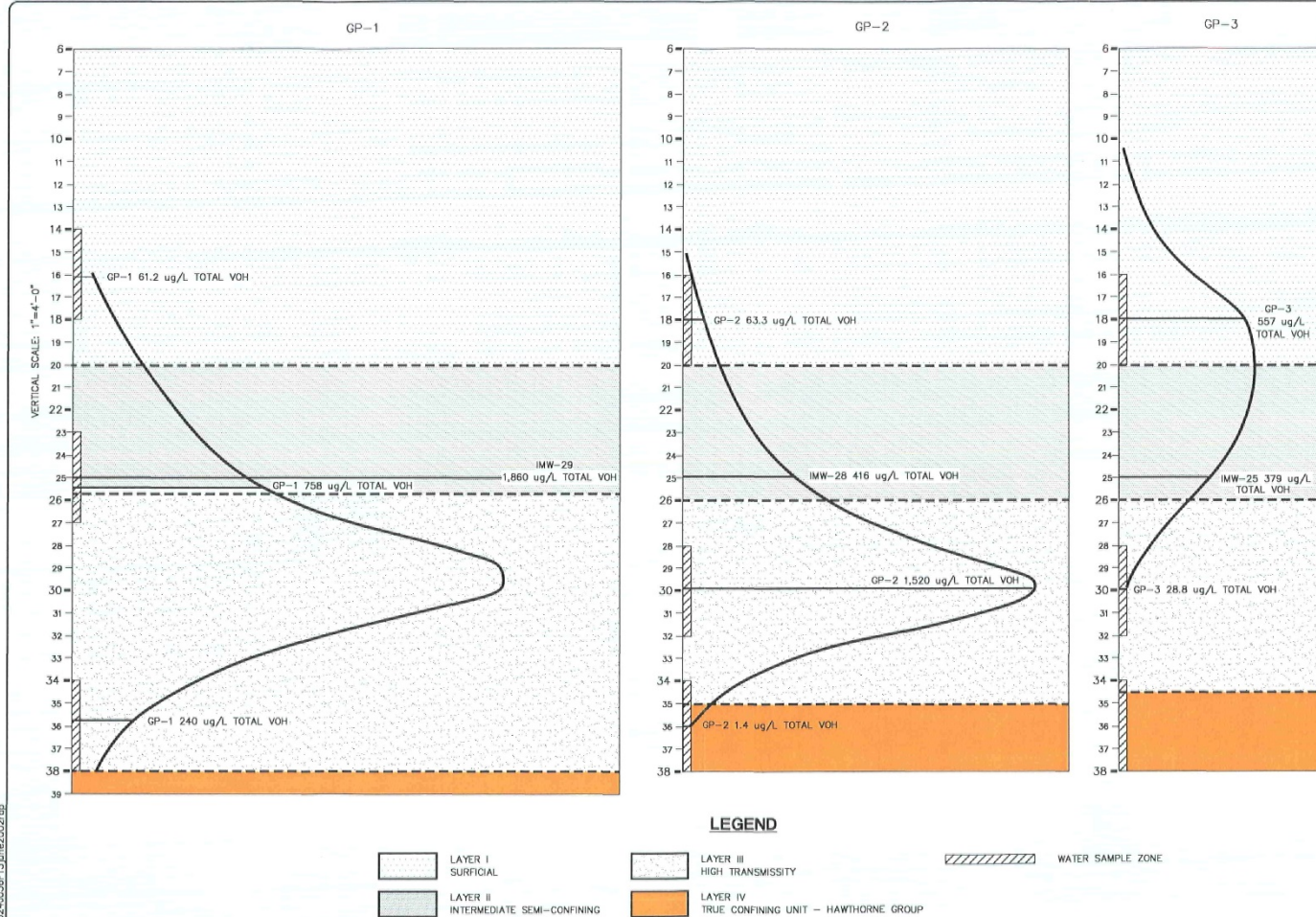


**ENVIRONMENTAL SERVICES**  
4400 N. 140th AVENUE NORTH  
SUITE 100  
CLEARWATER, FLORIDA 34622

|               |                |                      |
|---------------|----------------|----------------------|
| DRAWN BY: KES | SCALE: NOTED   | PROJ. NO.: 552-4J056 |
| CHKD. BY:     | DATE: 10/28/97 | DWG.: 10             |

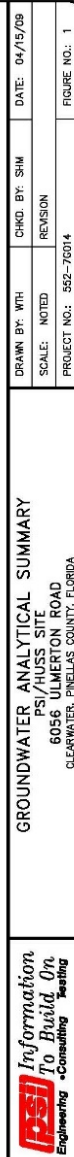
NOTE:  
LITHOLOGIC UNIT BOUNDARIES ARE DASHED WHERE INFERRED.

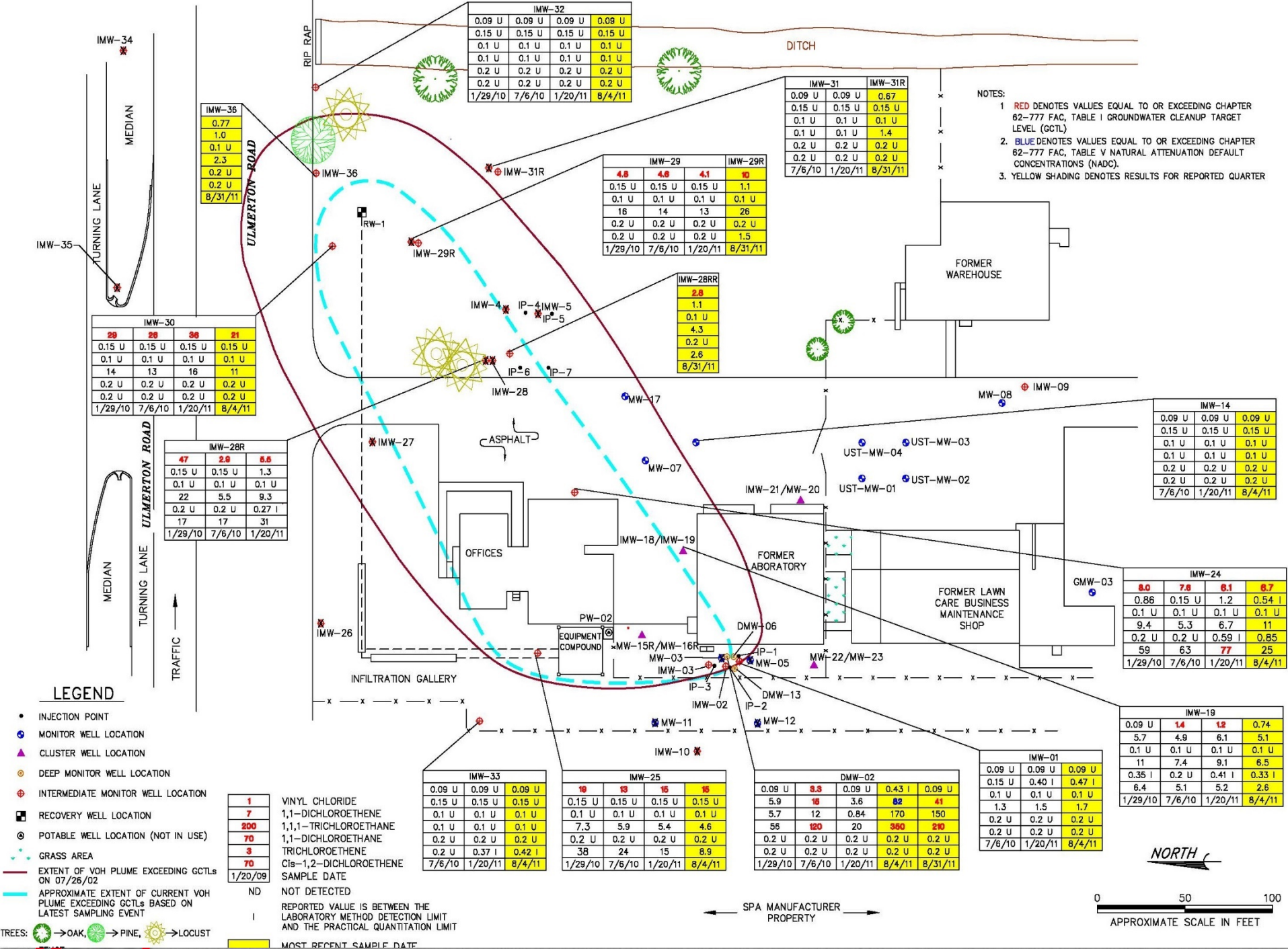
# Cross Section VOH Plume



|                                                                            |               |                       |               |
|----------------------------------------------------------------------------|---------------|-----------------------|---------------|
| DATE: 6/25/02                                                              | CHKD. BY: SBW | DRAWN BY: SBW         | FIGURE NO.: 5 |
| REVISION                                                                   | N.T.S.        | PROJECT NO.: 552-4056 |               |
| CONTAMINANT VERTICAL PROFILE CROSS-SECTIONS                                |               |                       |               |
| PSI/HUSS SITE<br>6056 HAWKERS ROAD<br>CLEARWATER, PINELLAS COUNTY, FLORIDA |               |                       |               |
| <b>Information To Build On</b><br>Engineering • Consulting • Testing       |               |                       |               |

P:\552-Env\2007\G- Reports 2007\7G014 HUSS\CAD\Year B\Year B Qtr 2.dwg





# Current Site Conditions



Knight Enterprises

# Current Site Conditions

Spa Manufacturing



# Remedial Strategies

## 1. Pump and Treat

- at source well – reduced 1,1,1-TCA
- Pump and Treat at downgradient edge – concern with off-site migration into DOT ROW widening project

## 2. Chem Ox ( $\text{KMnO}_4$ ) - 2 pilot tests during 2 episodes – Reduced plume

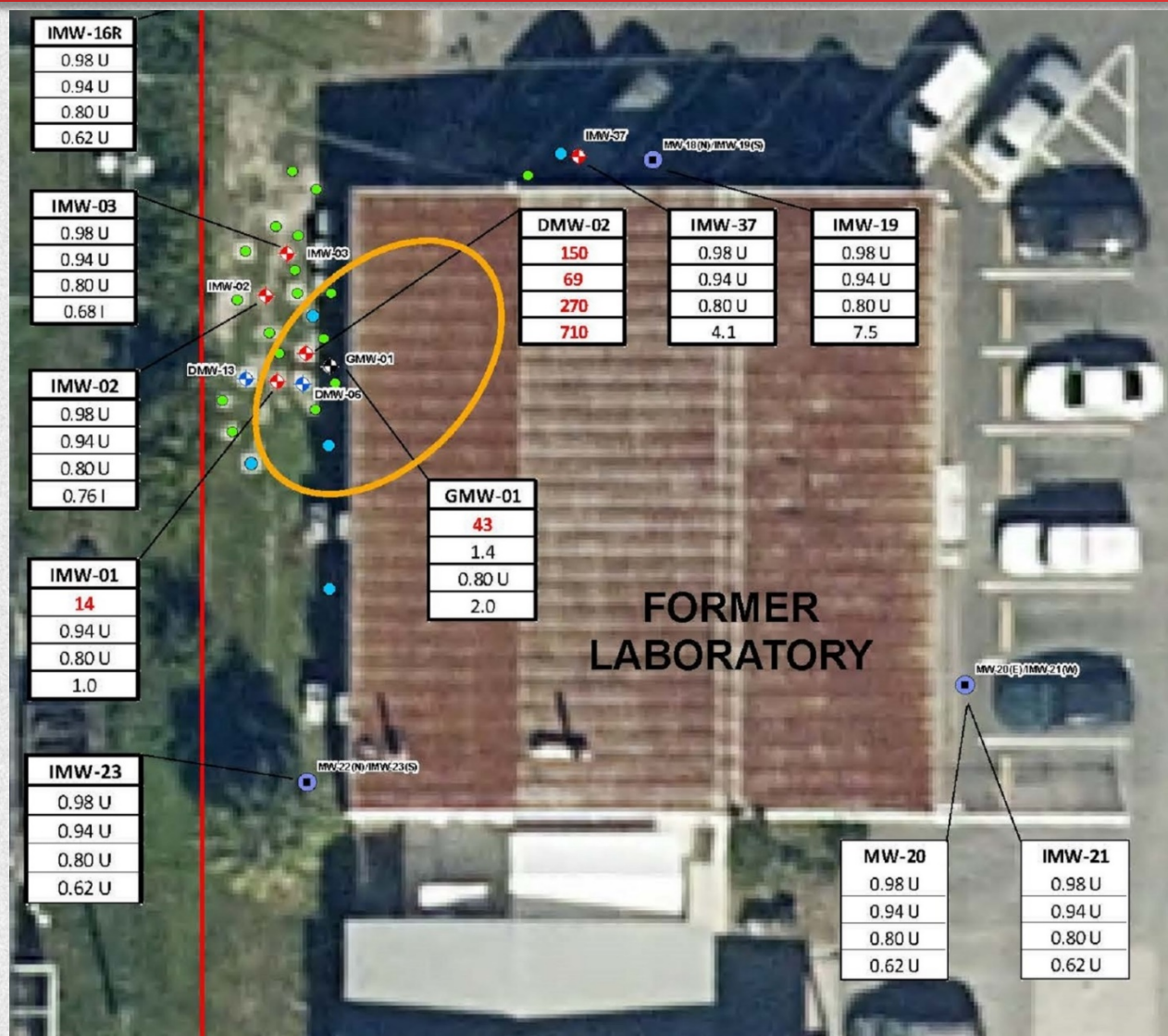
## 3. Monitored Natural Attenuation

# Closure Strategy

- 1,1,1-TCA concentrations reduced from 22,830 ug/L to 200 ug/L at source well (>99% reduction)
- Vinyl chloride plume stable (350 feet length), mostly single digit range, several wells in double digit range
- Y2013 - Stable GW Plume
- FDEP granted approval for a “Conditional Closure”
- Not accepted by site owner

# Plume Concentrations

| Analyte      | GCTL<br>ug/L | NADC<br>ug/L |
|--------------|--------------|--------------|
| Chloroethane | 12           | 1200         |
| 1,1-DCE      | 7            | 70           |
| 1,1,1-TCA    | 200          | 2000         |
| 1,1-DCA      | 70           | 700          |



# Vinyl Chloride Contour



# Biogeochemical Reductive Dehalogenation

- BiRD – process of stimulating abiotic reduction of chlorinated solvents by forming reactive iron sulfides.
- Application requires presence of sufficient carbon source, sulfate and iron.
- Carbon and sulfate usually must be added, and sometimes iron.

# Biogeochemical Reductive Dehalogenation

- 3 step process
  1. Stimulate common sulfate-reducing soil bacteria (Biologic sulfate reduction)
  2. Facilitates conversion of native iron into iron sulfides. (Geochemical mineral formation)
  3. Iron sulfides can reduce CAHs (Dechlorination)

# Biogeochemical Reductive Dehalogenation

## Advantages:

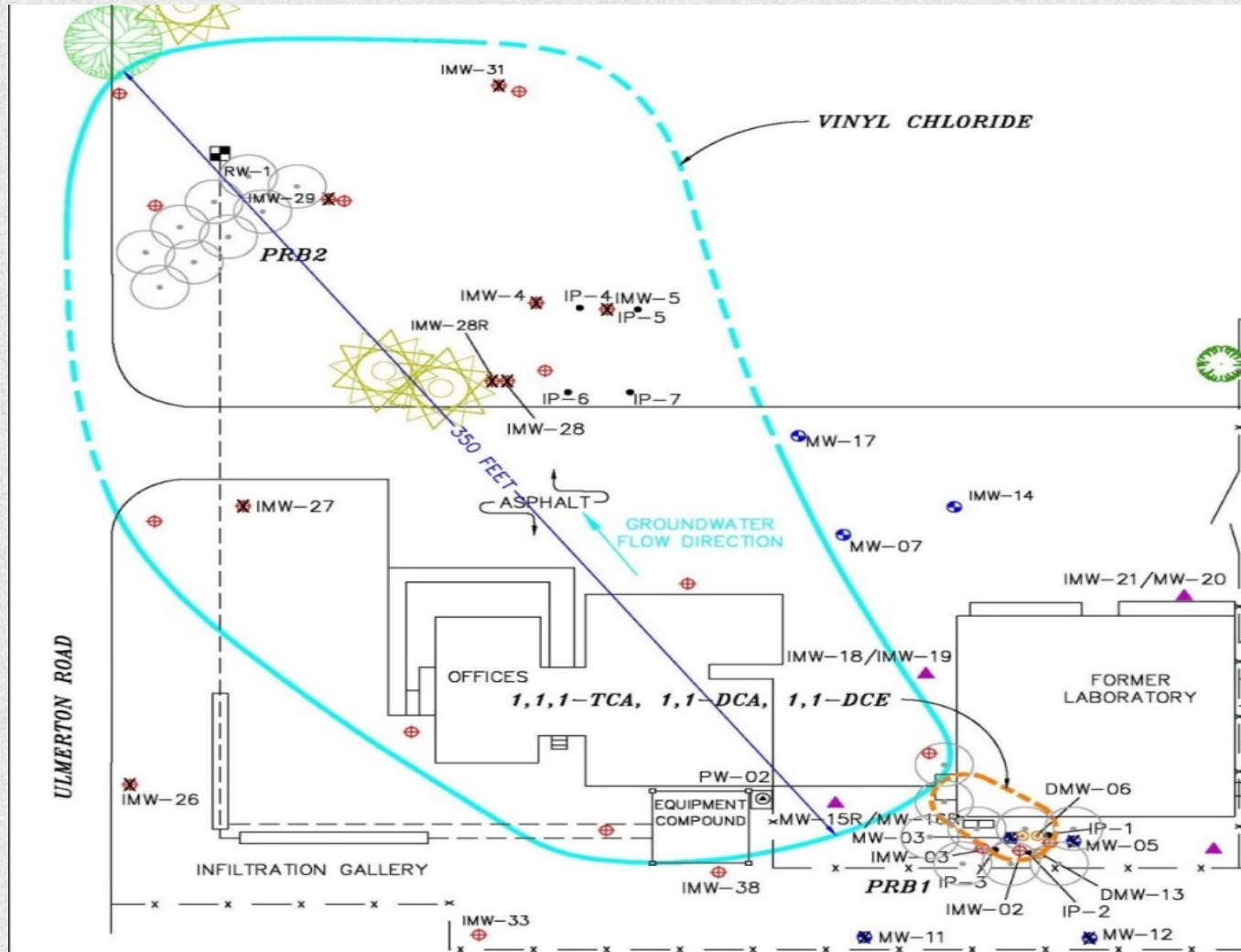
- Sulfate bacteria – ubiquitous
- Simple sulfate reduction
- Fast acting (instantaneous) – Hours to days to weeks)
- Little daughter products
- Inexpensive

# Biogeochemical Reductive Dehalogenation

Disadvantage:

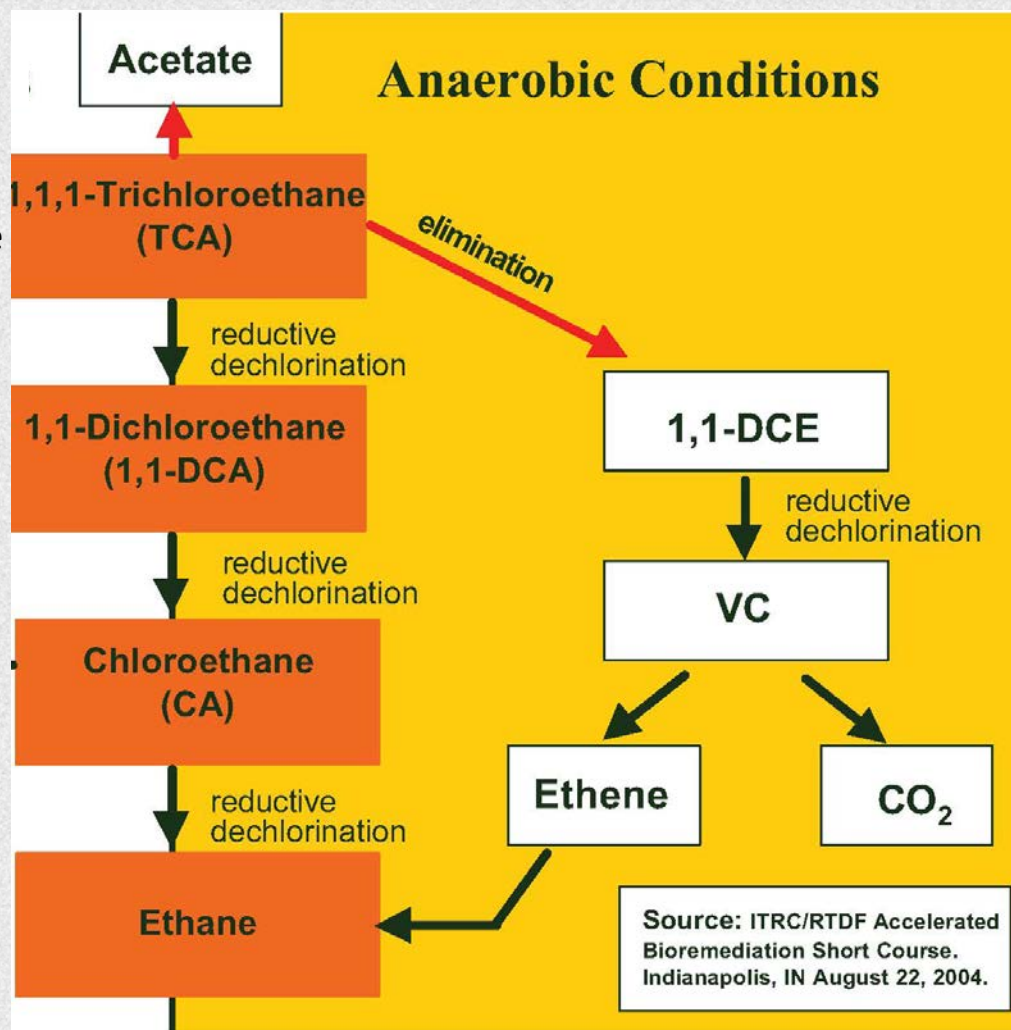
- New technology
- Limited engineering guidance available
- Several mechanism must occur simultaneously

# Y2013 GW 1,1,1-TCA and VC Plume

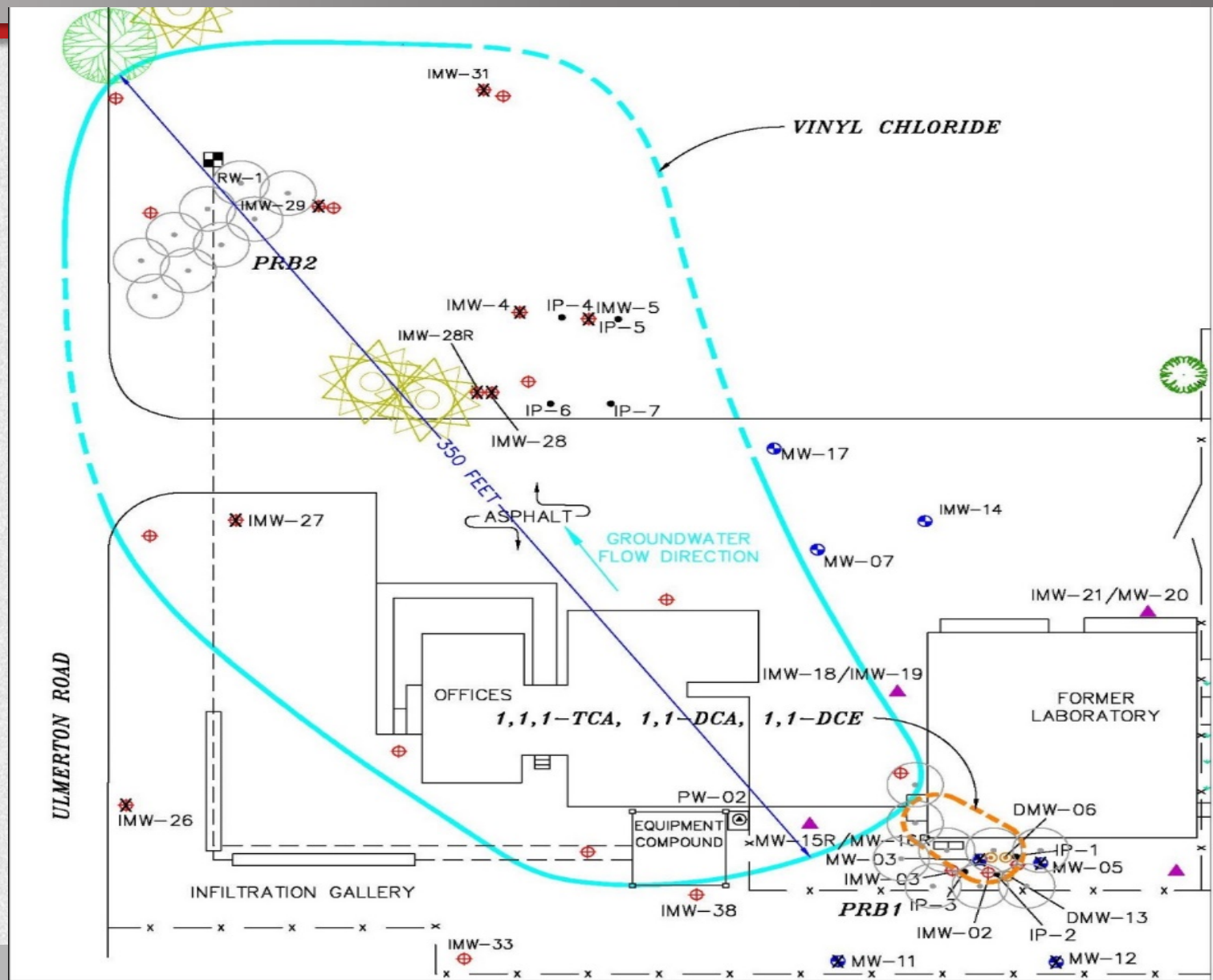


# Solution/Hypothesis

- Lines of evidence to suggest BiRD was occurring at the site
  - Evidence of pyrite in soil samples analyzed by XRD/XRF
  - Evidence of 1,1-DCA – several literature sources suggest 1,1-DCA is a product of abiotic degradation of 1,1,1-TCA on FeS minerals (Gardner et al., 2002, Butler and Hayes, 2000, Choi et al., 2009)
- Choi et al. (2009) also suggested the reduction of 1,1,1-TCA by FeS was further reduced in the presence of hydrogen sulfide concentrations. (Fundamental of biogeochemical reduction)
- Also a persistent, large area plume of low level vinyl chloride, believed to be result of anaerobic gw conditions and resultant 1,1-DCE degradation.
- Enhanced biological reduction was considered, but unsure significant reducing conditions could affect vinyl chloride



# Pilot Test Injection Areas



# BiRD Injection Chemicals

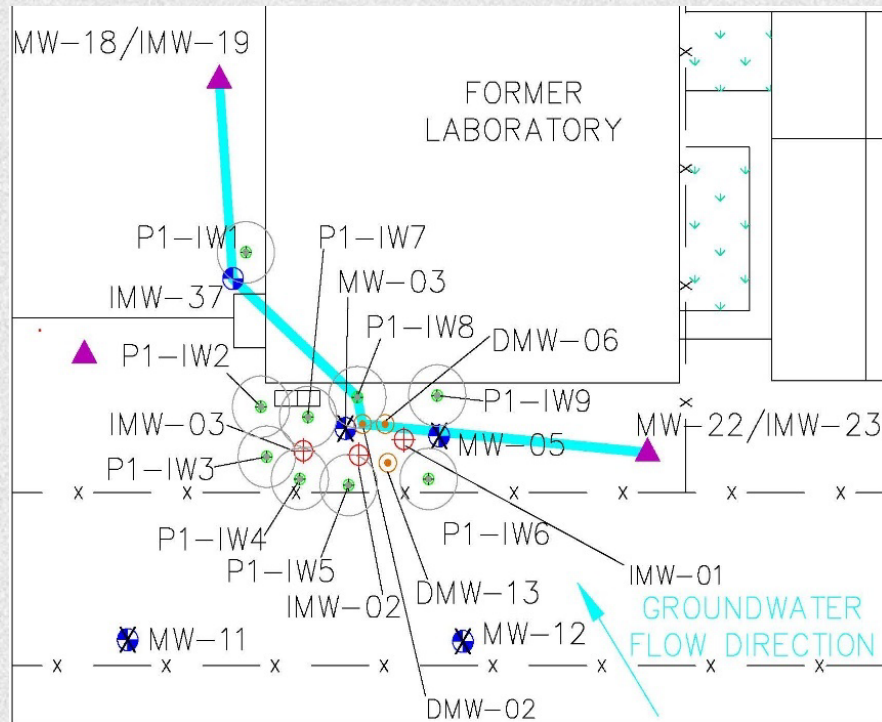
PRB1: Target FeS goal of 50 mg/kg, general carbon to sulfate ratio of 0.67

PRB2: Promote strong sulfate reduction, target 3,000 mg/L SO<sub>4</sub>

|                                 | PRB1 (1,1,1-TCA)                             | PRB2 (vinyl chloride)                        |
|---------------------------------|----------------------------------------------|----------------------------------------------|
| Ferrous Sulfate (\$0.50/lb)     | 15 lbs/IW → 135 total lbs                    | 40/IW → 360 total lbs                        |
| Epsom Salt (\$0.50/lb)          | 40/IW → 360                                  | 320/IW → 2,880                               |
| Sodium Lactate (\$10.00/gallon) | 9 gal /IW → 81 total gal (~891 lbs)          | 15/IW → 135 (~1,485 lbs)                     |
|                                 | 1000 gallons of oxygen free water per point. | 1000 gallons of oxygen free water per point. |




# Injection Layout - PRB1

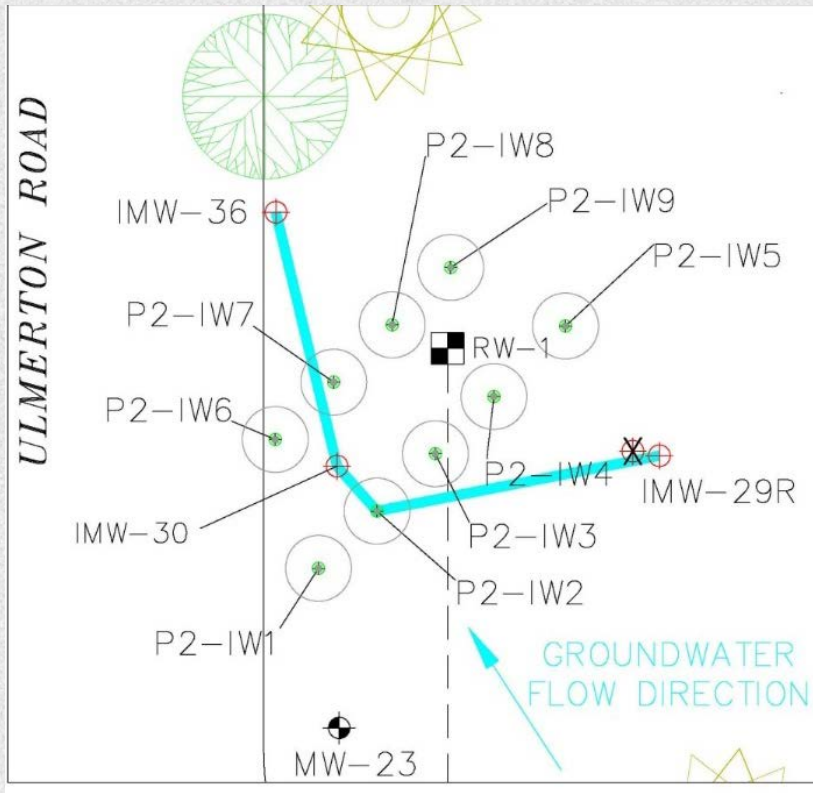


9 Permanent IW points at each PRB – screened 15 to 30 feet bls

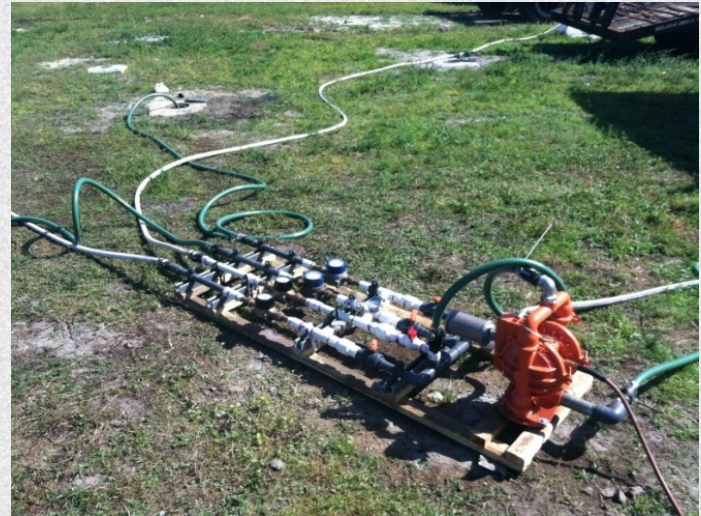


Injection Rate: 0.4 to 6 gpm at pressures of 10 to 65 psi

# Injection Layout – PRB2

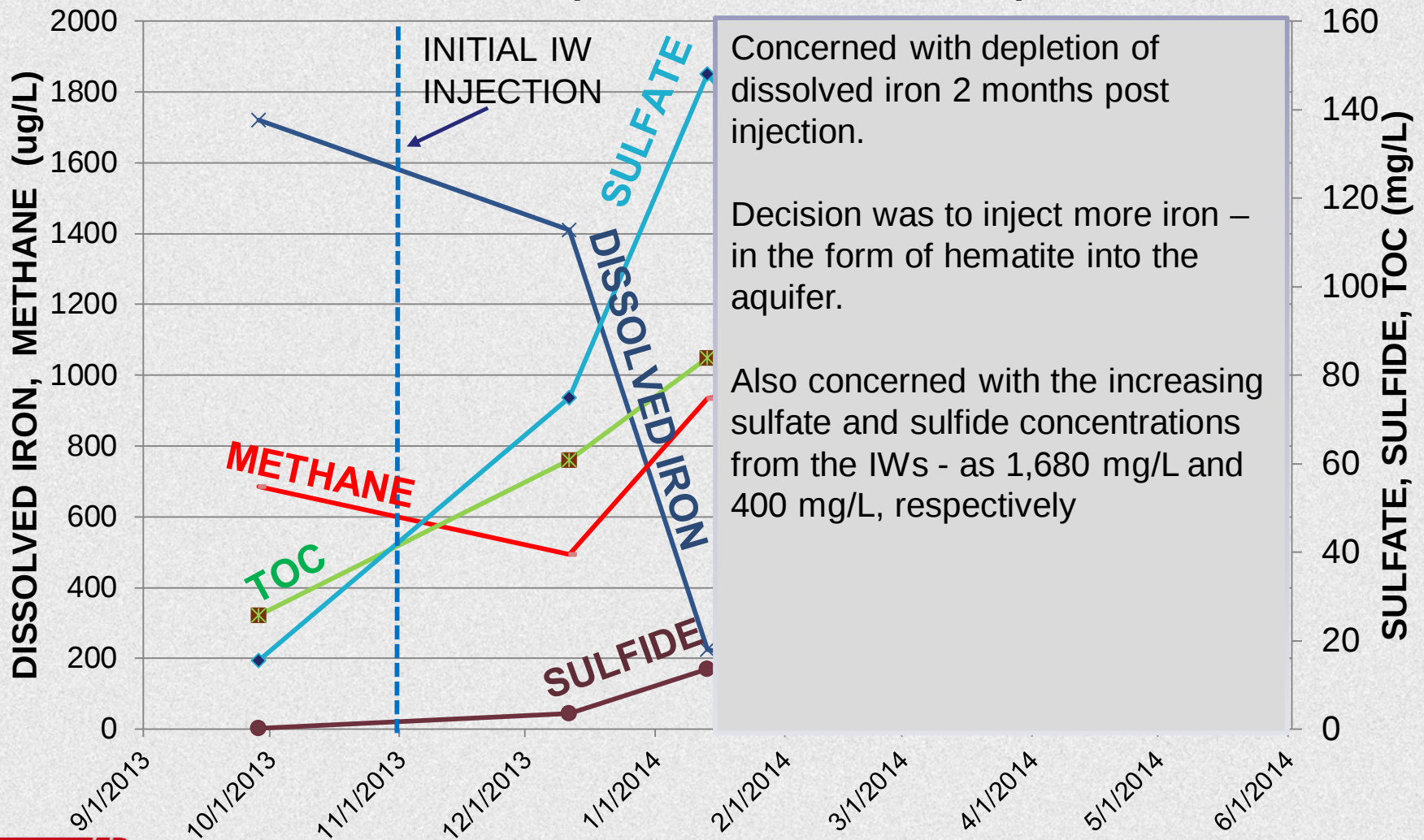


# Injection Process

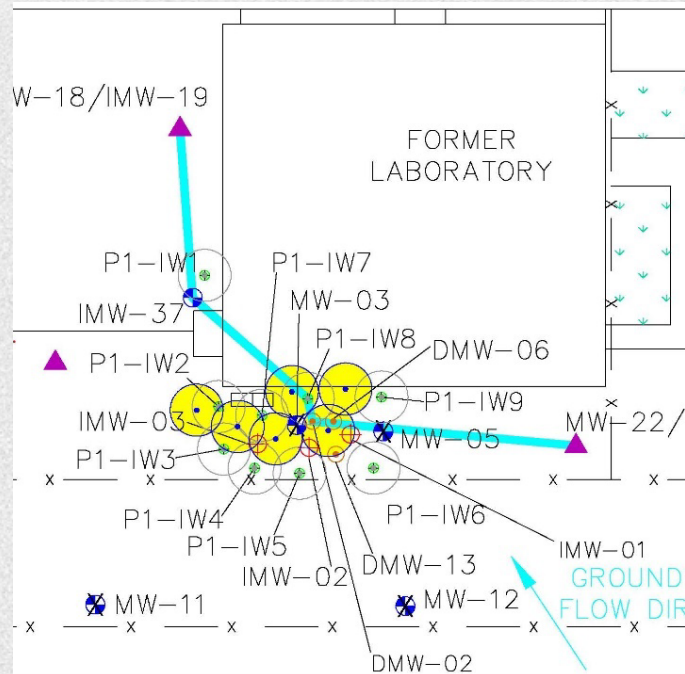


# PRB1 Geochemistry Results

## DMW-02 (SOURCE 1,1,1-TCA MW)

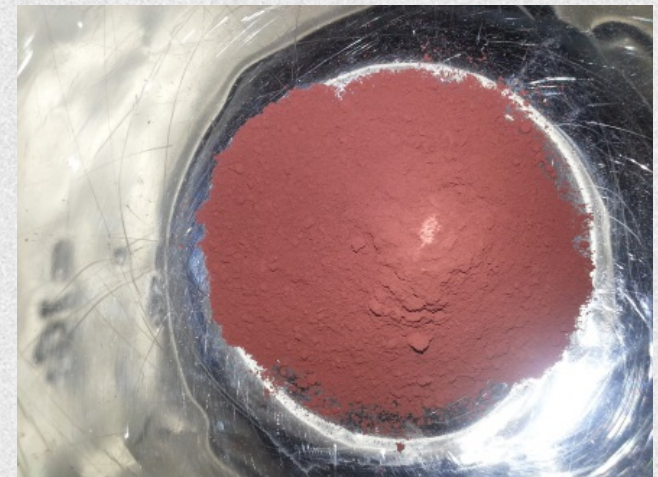


# PRB1: DPT Injection with Hematite



DPT injection Interval:

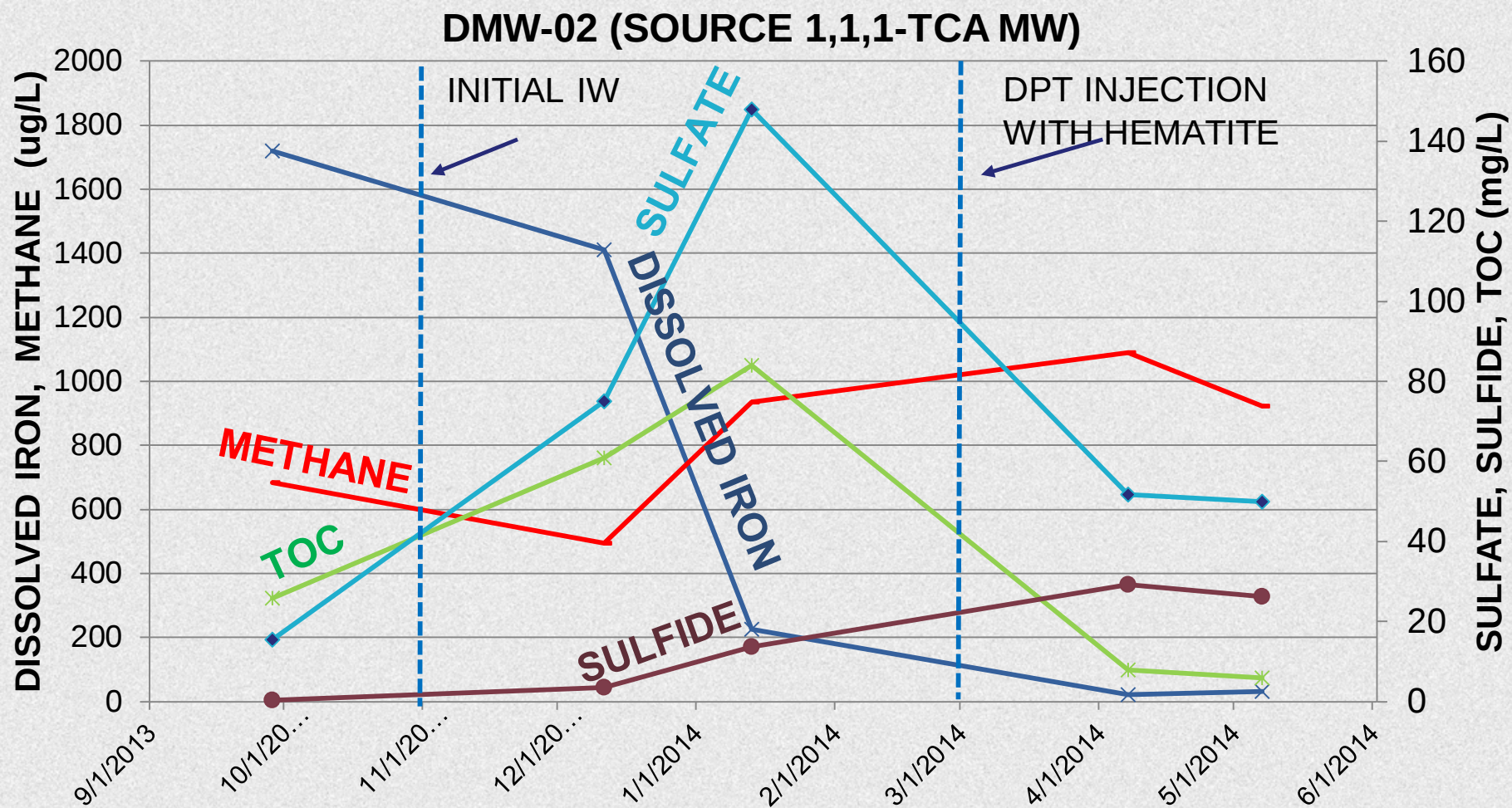
- 28-32 feet bls,
- 22-26 feet bls
- ½ original design volume of chemicals,
- added 2 pounds of hematite
- 125 gallons of oxygen free water,
- 125 gallons of pore water push.



# DPT Injection Process

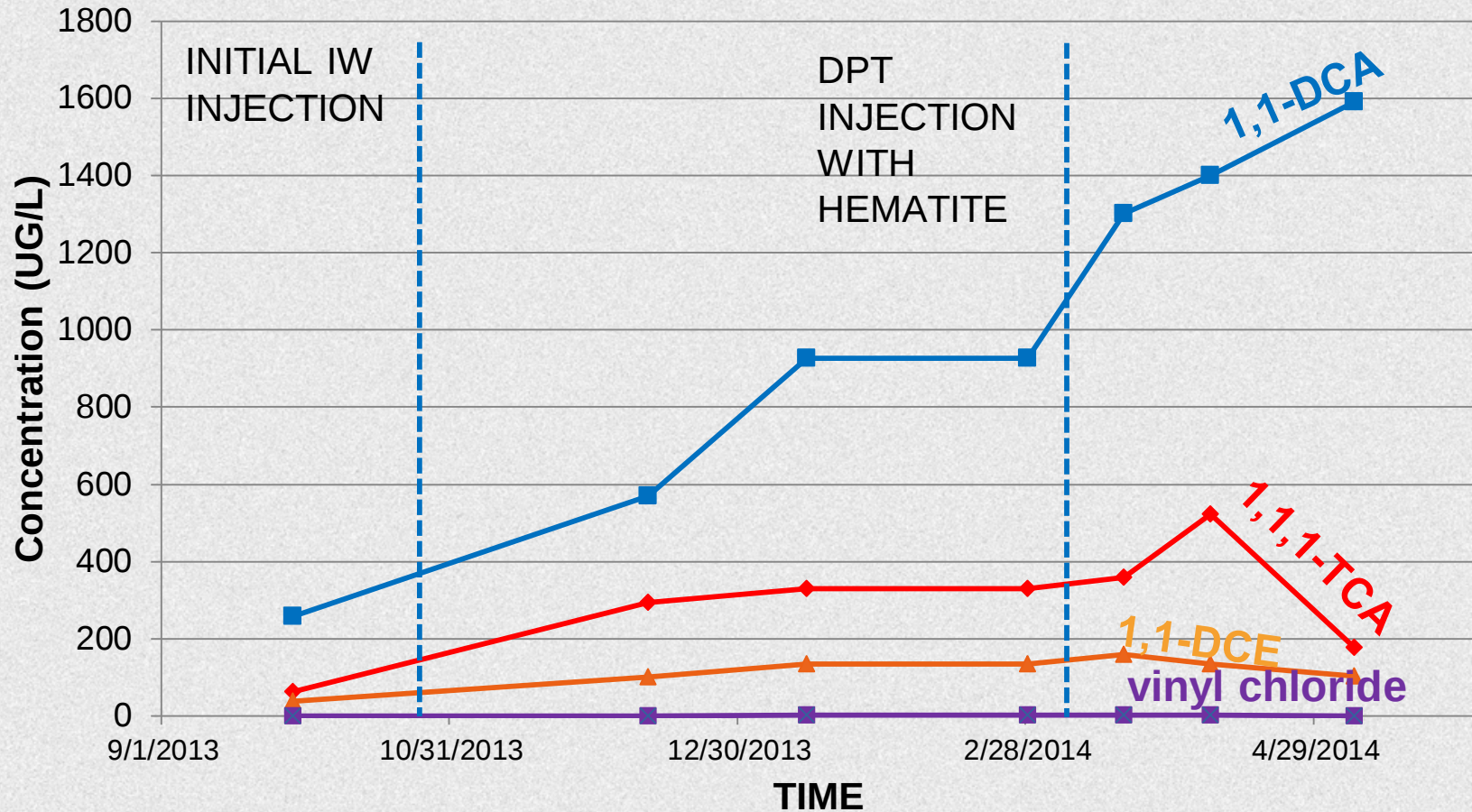


# PRB1 Results After Injection of Hematite

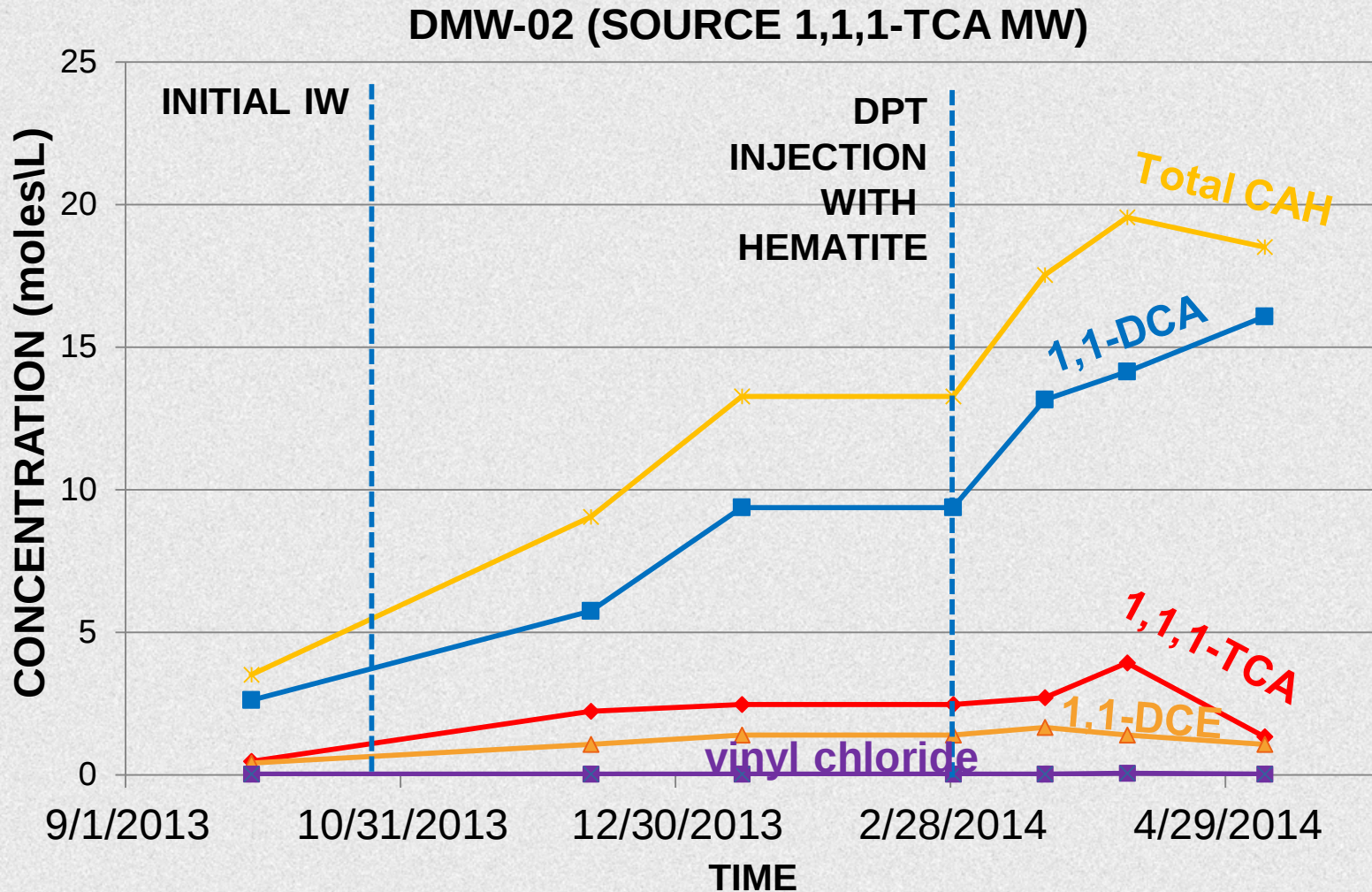


# DMW-02 Contaminant Concentrations

DMW-02 (SOURCE 1,1,1-TCA MW)



# DMW-02 Contaminant Concentrations (moles/L)

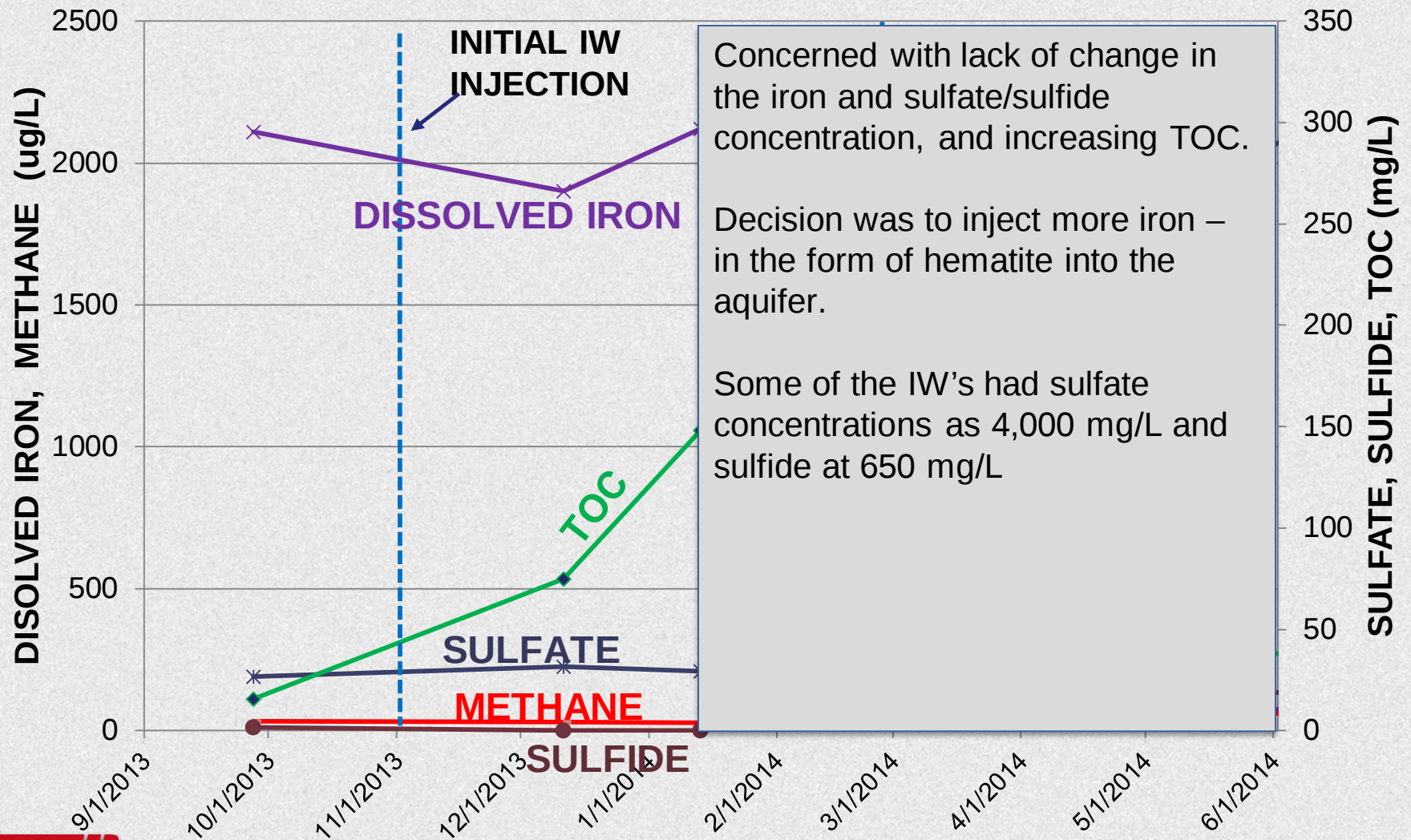


# Black Particulates Formed in Groundwater

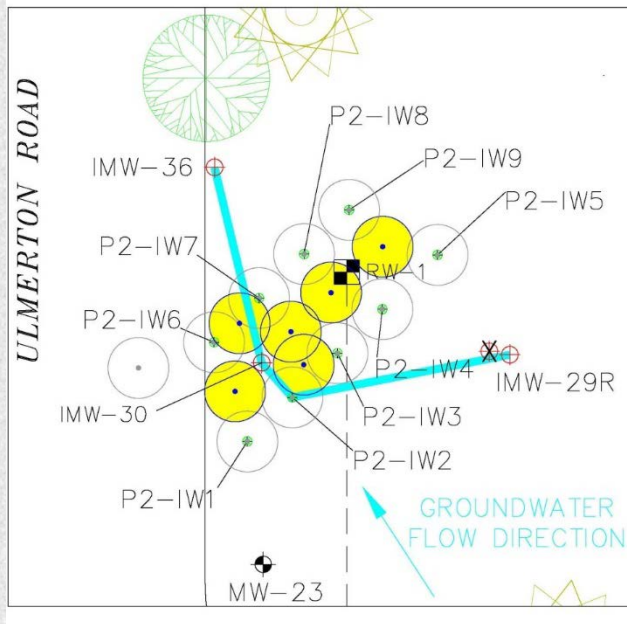


# PRB2 (Vinyl Chloride Area) Geochemistry Results

## MW-30 (DOWNGRADIENT VINYL CHLORIDE AREA)

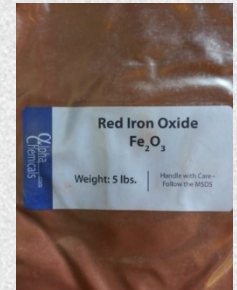
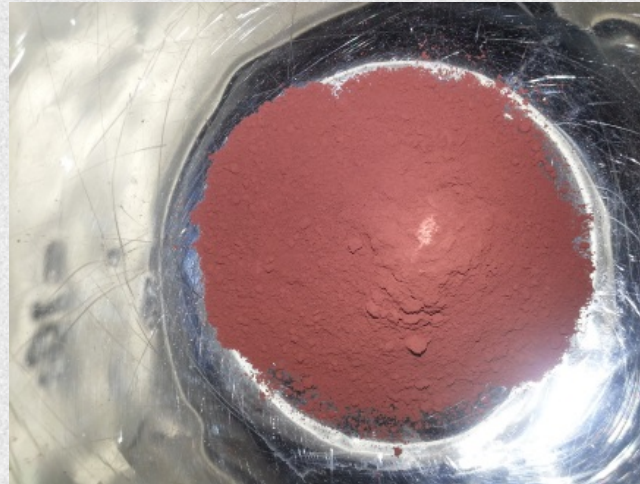


# PRB2 DPT Injection Point Layout

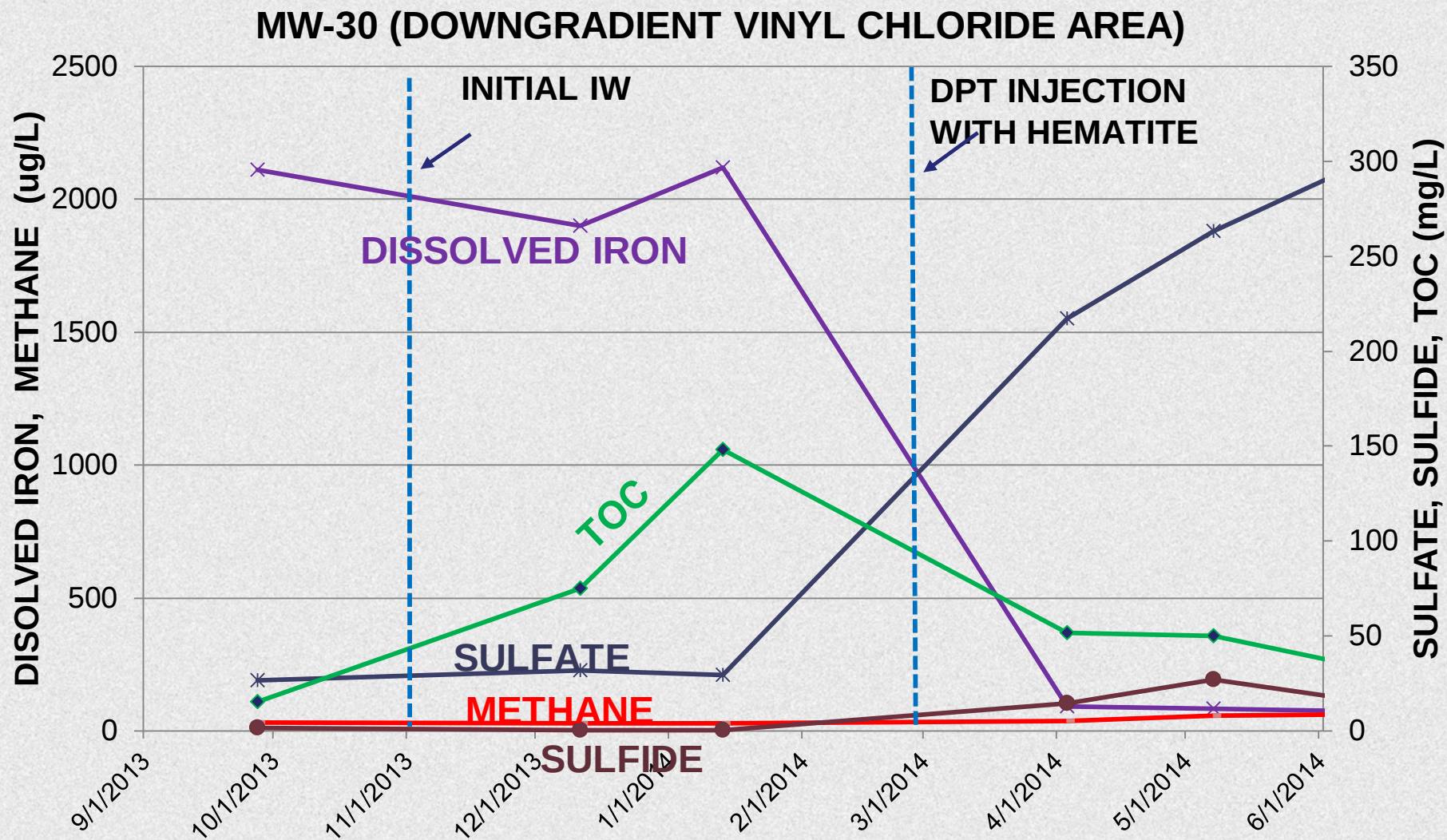


DPT injection:

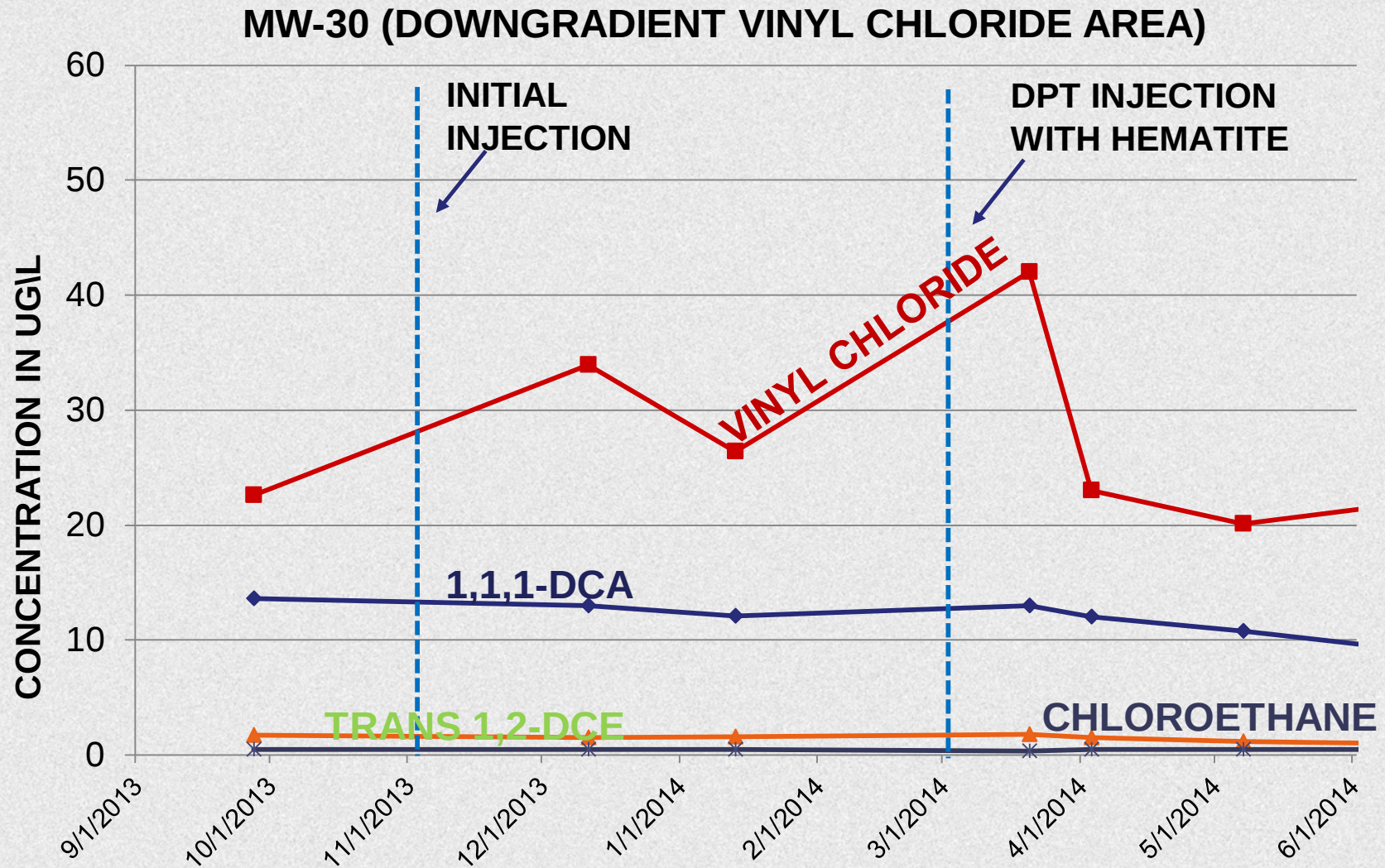
- 28-32 feet bls
- 22-26 feet bls,
- ½ original design volume of chemicals,
- added 2 pounds of hematite
- 125 gallons of oxygen free water
- 125 gallons of pore water push.



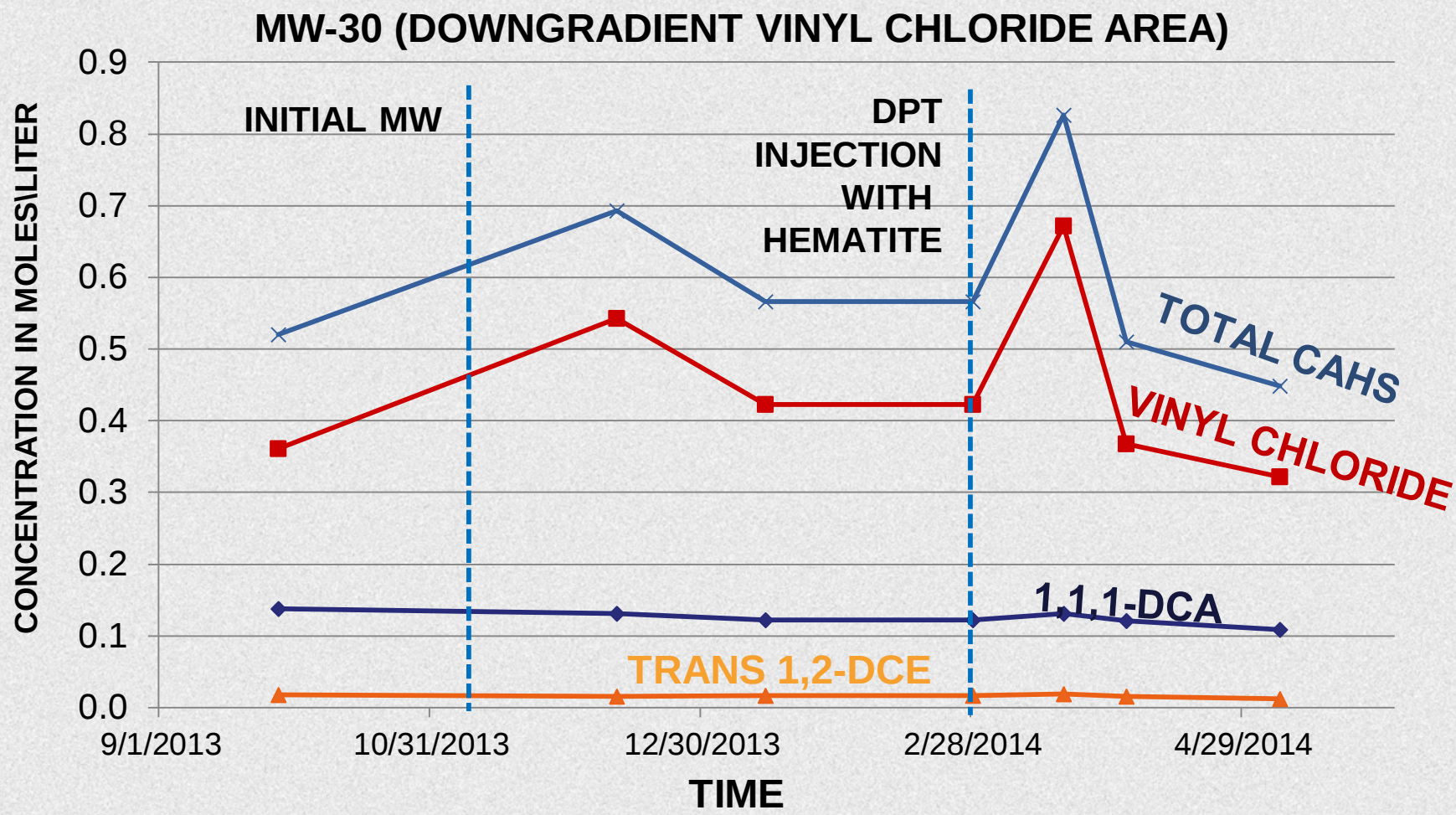
# PRB2: Results After DPT Hematite Injection



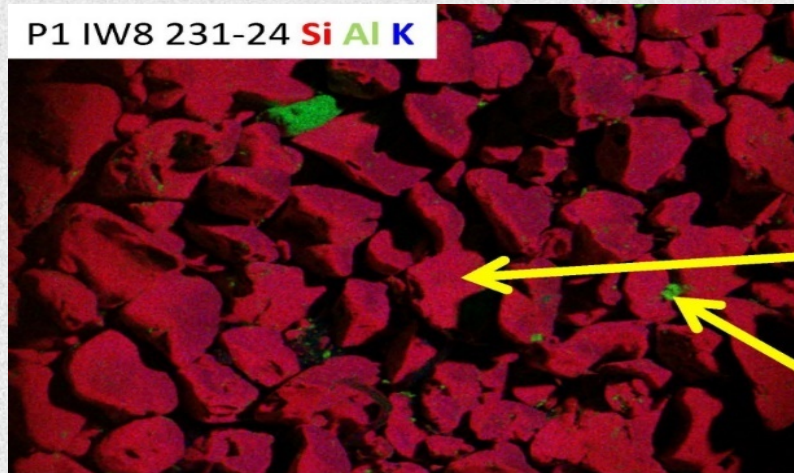
# MW-30 Contaminant Concentrations (ug/L)



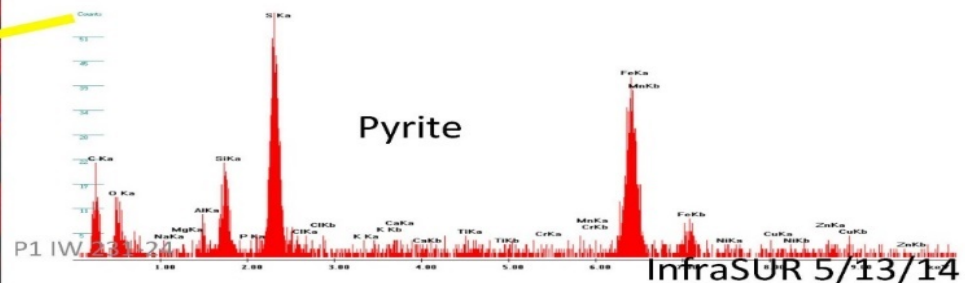
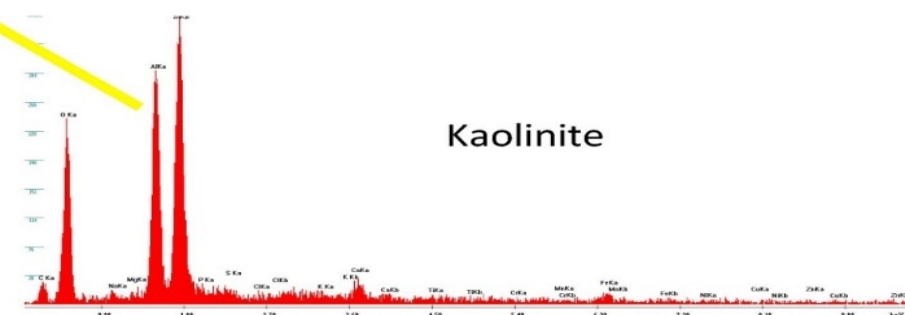
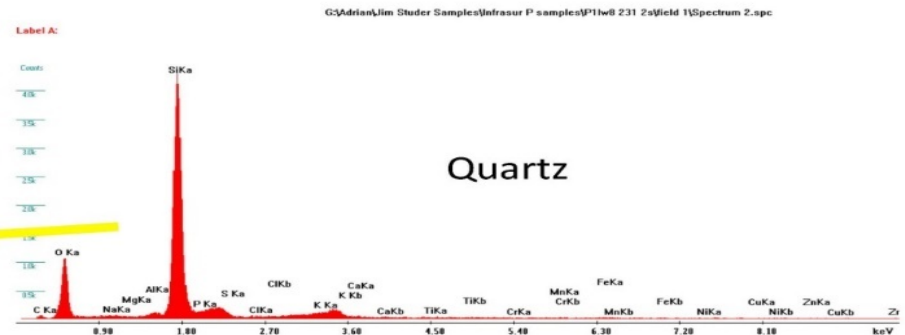
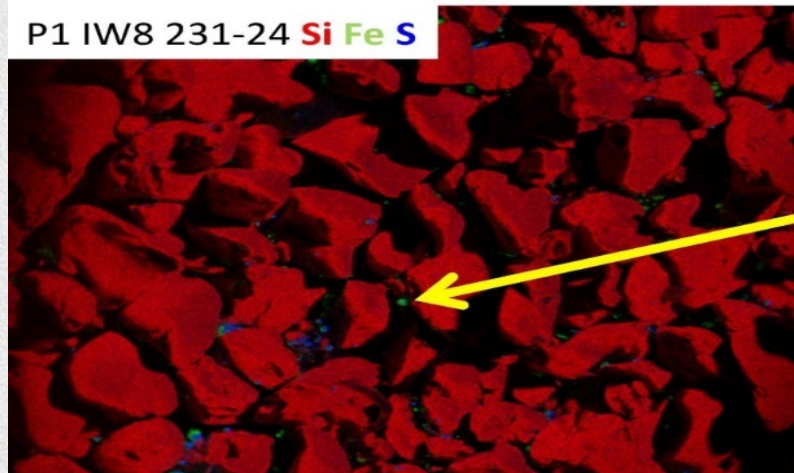
# MW-30 Contaminant Concentration (Moles/Liter)



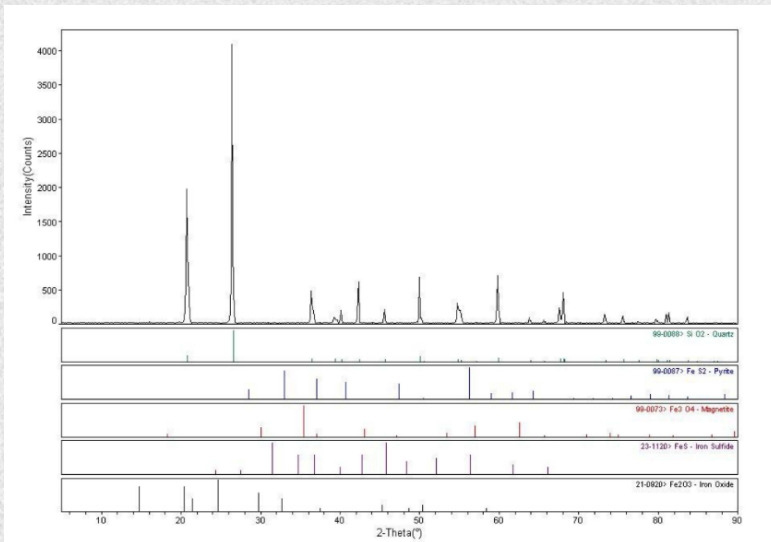
# PRB1: X-RAY Spectroscopy Pre-injection (EDS)



FOV = 1.764 mm



# PRB1: Post Injection XRF/XRD



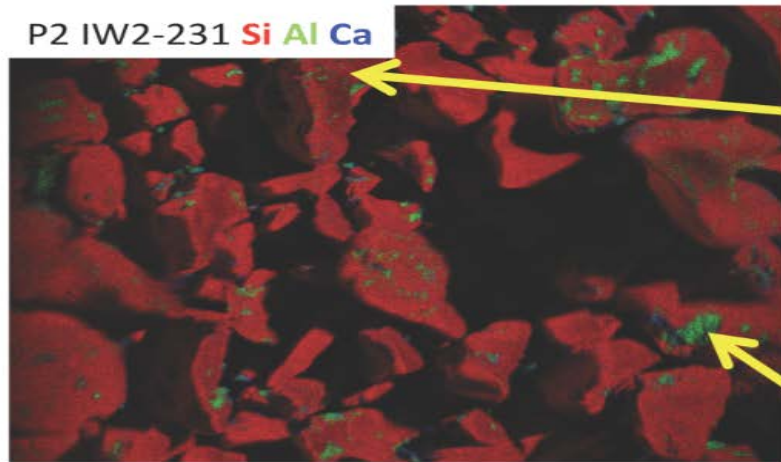
- X-ray fluorescence (XRF) spectrometry identified iron and sulfur in sample.
- X-ray diffraction (XRD) did not detect iron oxide or iron sulfide within the detection limits.

Evidence of iron and sulfur  
in sample

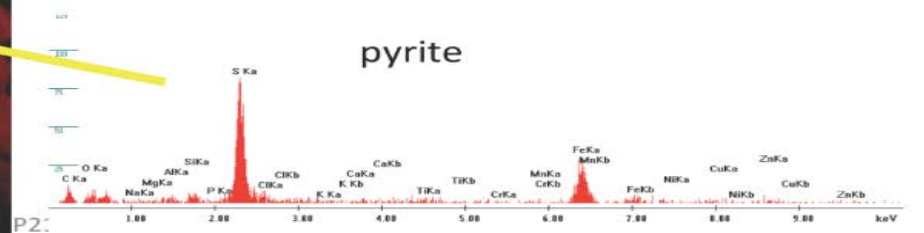
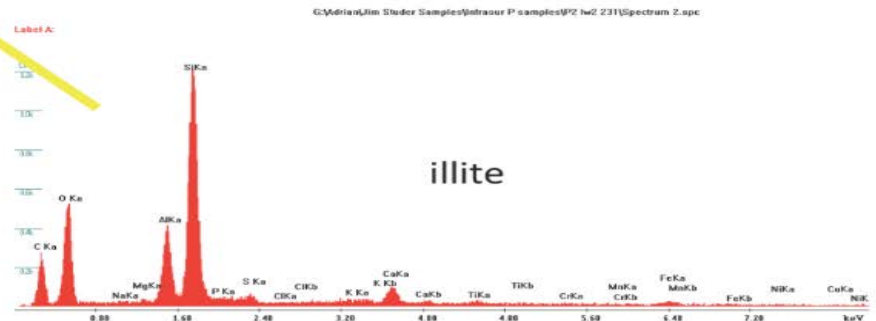
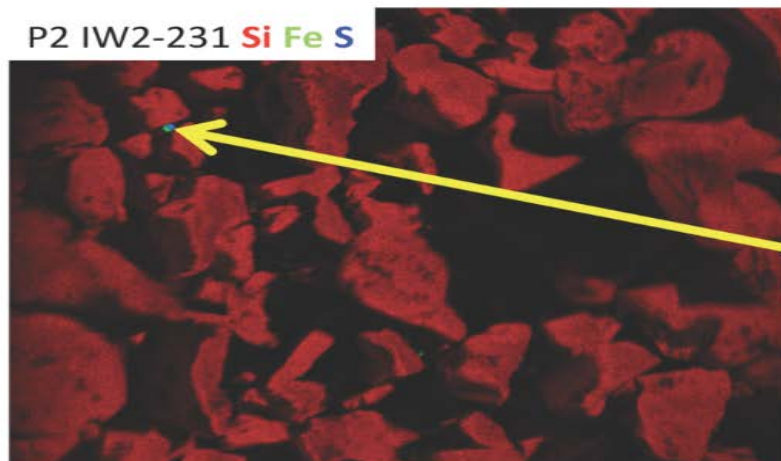
Table 1. Results for elemental analysis by XRF

| Sample Number:<br>Sample Description | SB1, 22ft<br>Soil    |                           |
|--------------------------------------|----------------------|---------------------------|
| Oxide                                | Concentration<br>%wt | Limit of Detection<br>%wt |
| SiO <sub>2</sub>                     | 73.06                | 0.01819                   |
| Al <sub>2</sub> O <sub>3</sub>       | 12.8                 | 0.01401                   |
| CaO                                  | 6.05                 | 0.00470                   |
| SO <sub>3</sub>                      | 4.94                 | 0.00971                   |
| Fe <sub>2</sub> O <sub>3</sub>       | 1.11                 | 0.00280                   |
| TiO <sub>2</sub>                     | 0.694                | 0.00512                   |
| P <sub>2</sub> O <sub>5</sub>        | 0.39                 | 0.01123                   |
| Na <sub>2</sub> O                    | 0.36                 | 0.02405                   |
| K <sub>2</sub> O                     | 0.301                | 0.00402                   |
| MgO                                  | 0.23                 | 0.02268                   |
| ZrO <sub>2</sub>                     | 0.0687               | 0.00151                   |
| SrO                                  | 0.014                | 0.00112                   |

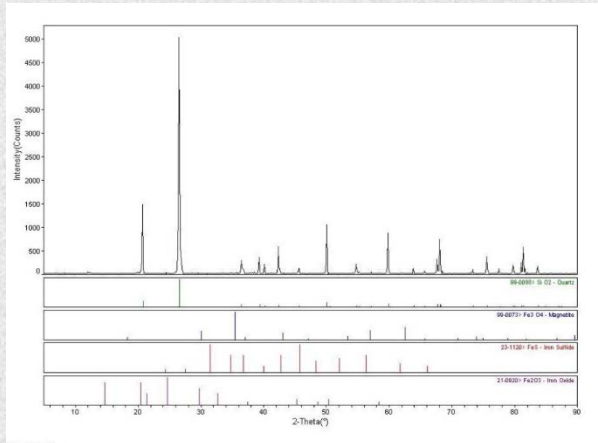
# PRB2 – Pre Injection, XRD – evidence of pyrite!



FOV = 1.764 mm



# PRB2: Post Injection XRF/XRD

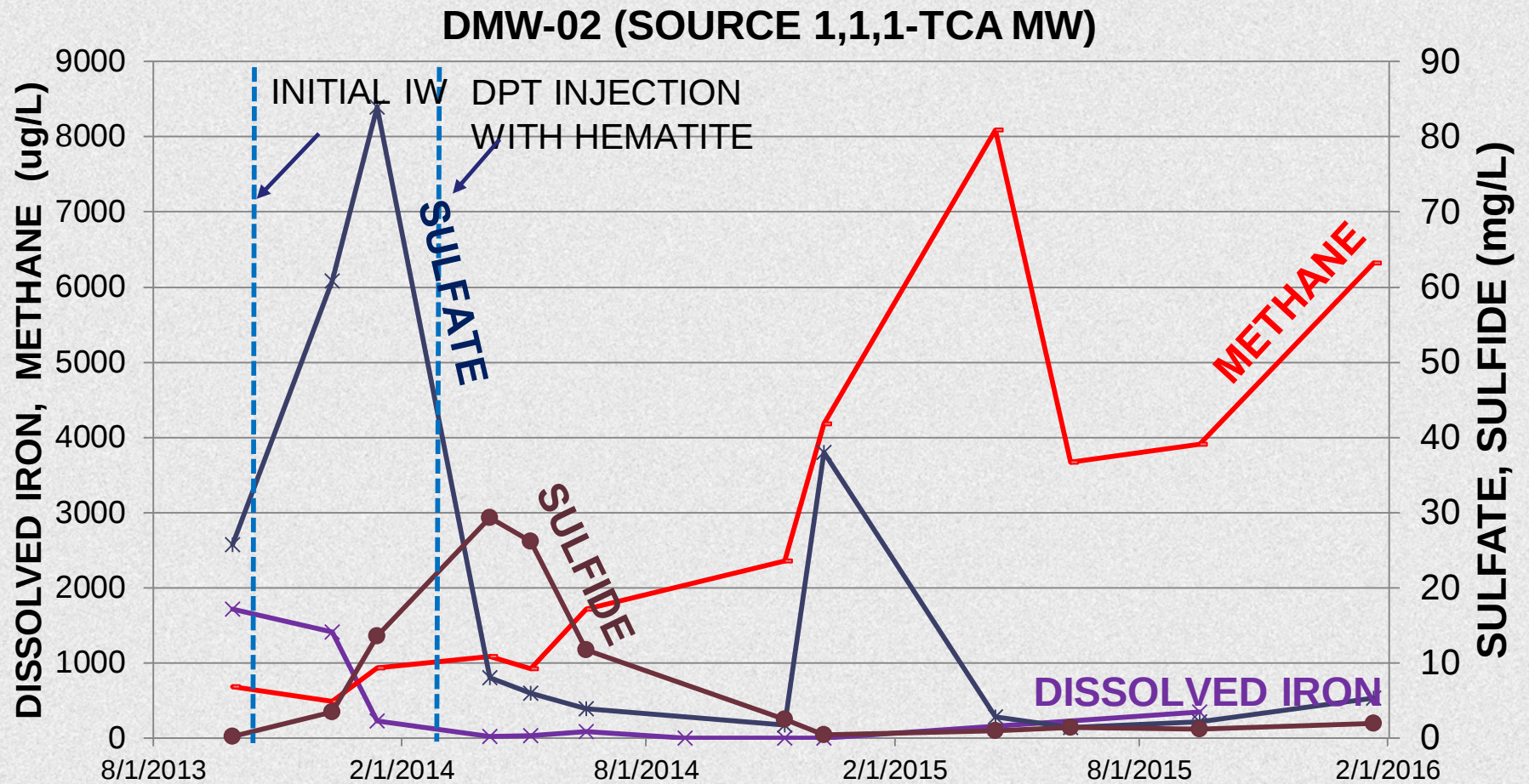


- X-ray fluorescence (XRF) spectrometry identified iron and sulfur in sample.
- X-ray diffraction (XRD) did not detect iron oxide or iron sulfide within the detection limits.

Table 2. Results for elemental analysis by XRF

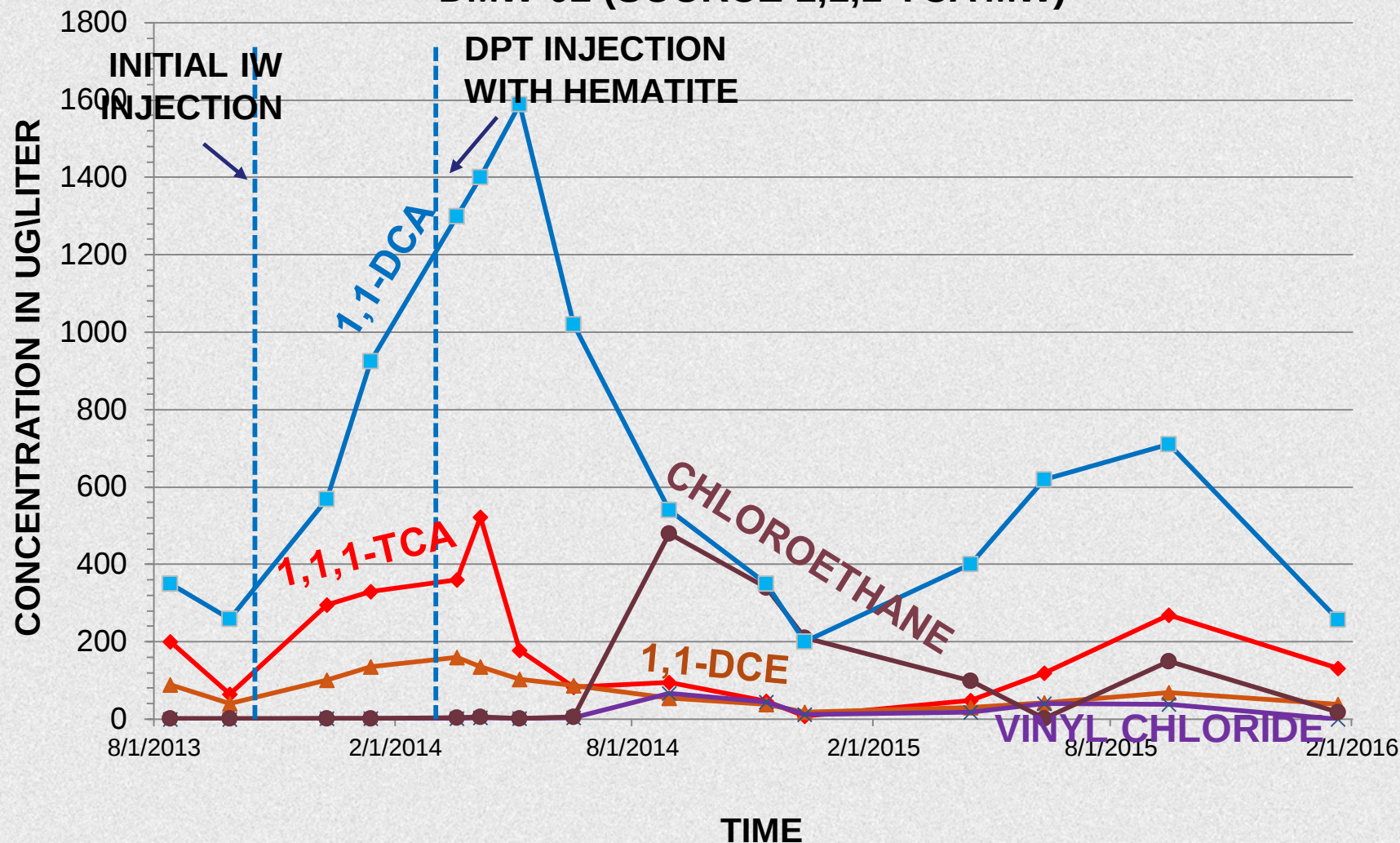
| Sample Number:<br>Sample Description | SB2, 24ft<br>Soil    |                           |
|--------------------------------------|----------------------|---------------------------|
| Oxide                                | Concentration<br>%wt | Limit of Detection<br>%wt |
| SiO <sub>2</sub>                     | 76.59                | 0.01902                   |
| Al <sub>2</sub> O <sub>3</sub>       | 16                   | 0.01552                   |
| SO <sub>3</sub>                      | 2.99                 | 0.00793                   |
| CaO                                  | 2.55                 | 0.00432                   |
| Fe <sub>2</sub> O <sub>3</sub>       | 0.628                | 0.00242                   |
| TiO <sub>2</sub>                     | 0.423                | 0.00448                   |
| P <sub>2</sub> O <sub>5</sub>        | 0.33                 | 0.00797                   |
| MgO                                  | 0.27                 | 0.02386                   |
| K <sub>2</sub> O                     | 0.153                | 0.00374                   |
| SrO                                  | 0.011                | 0.00098                   |
| ZrO <sub>2</sub>                     | 0.009                | 0.00130                   |

# 2016 – Post BiRD Geochemical Results



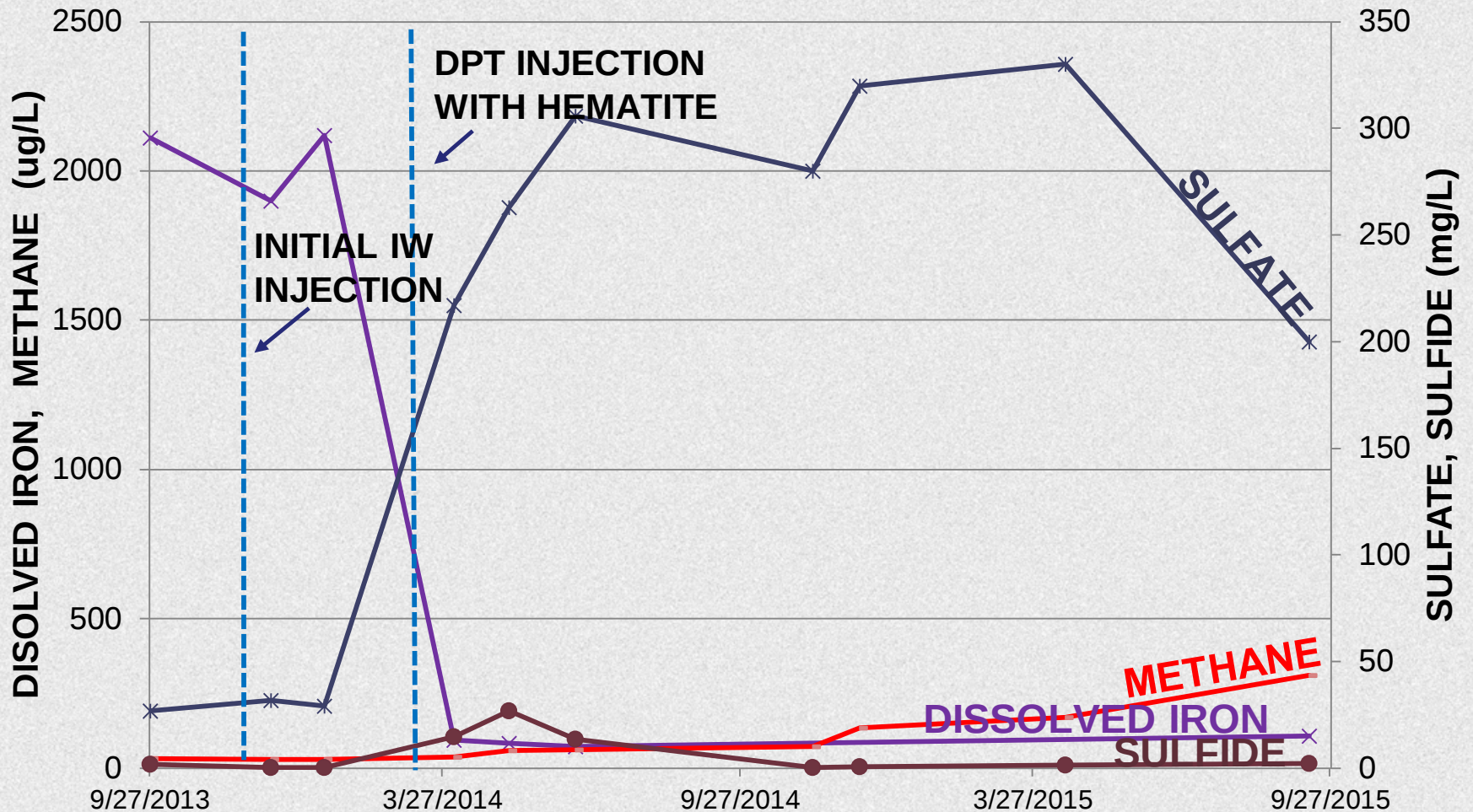
# 2016 – PRB1 Post BiRD Injection Results

DMW-02 (SOURCE 1,1,1-TCA MW)

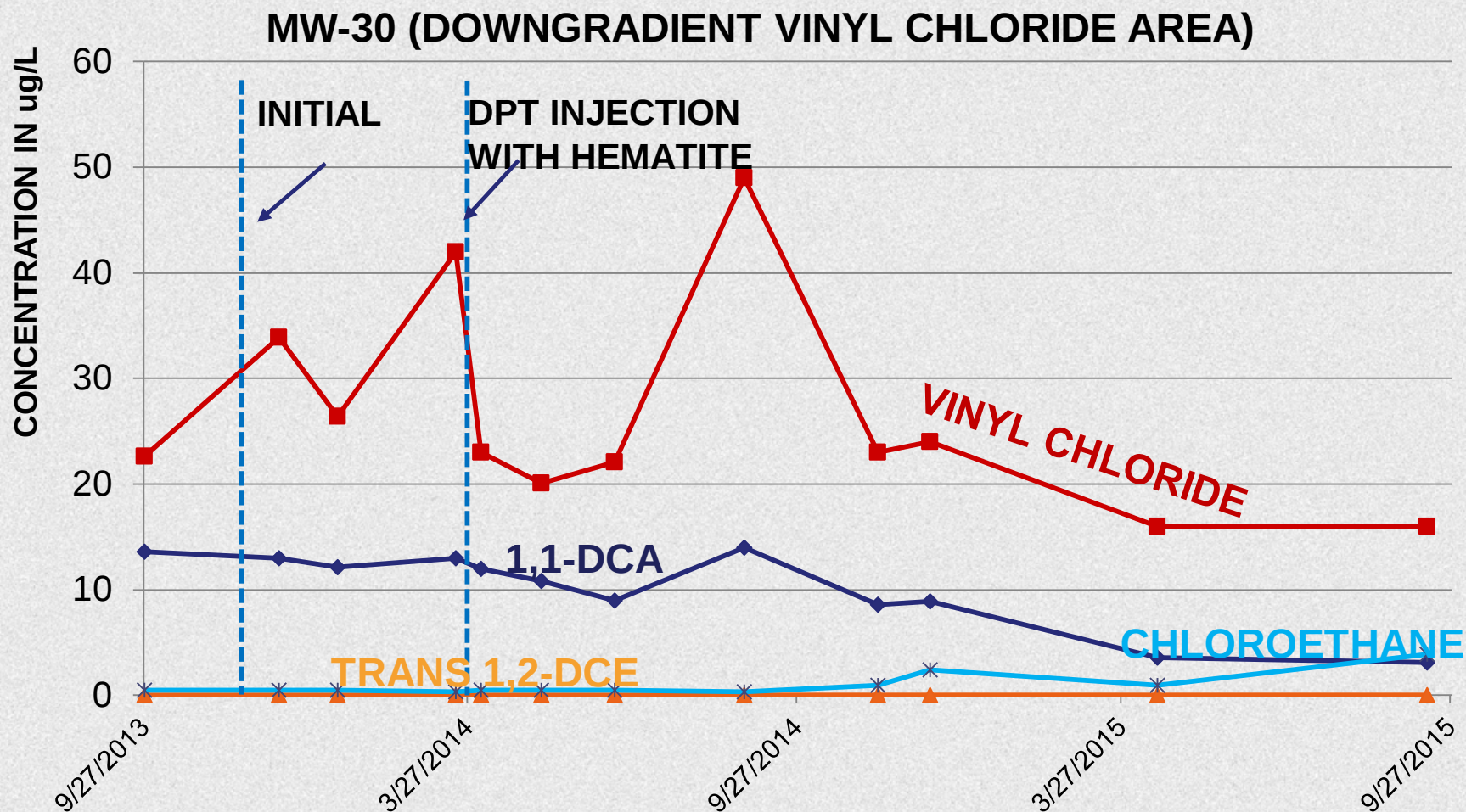


# 2015 - PRB2 Post BiRD Geochemical Results

## MW-30 (DOWNGRADIENT VINYL CHLORIDE AREA)



# 2015 – PRB2 Post BiRD Injection Results



# Post-BiRD Pilot Test Injection – PRB1 Source Area

## 1997 Data

| Monitor Well | 1,1,1-TCA ug/L | 1,1-DCA ug/L | 1,1-DCE ug/L | Chloro ethane ug/L | Vinyl chloride ug/L |
|--------------|----------------|--------------|--------------|--------------------|---------------------|
| GCTL         | 200            | 70           | 7            | 12                 | 1                   |
| NADC         | 2000           | 700          | 70           | 1200               | 100                 |
| Shallow      | 3,855          | 107          | 85           | <20                | <20                 |
| DMW-02       | 22,830         | 24,600       | 12,400       | <50                | 42                  |

## 2016 Data

| Monitor Well | 1,1,1-TCA ug/L | 1,1-DCA ug/L | 1,1-DCE ug/L | Chloro ethane ug/L | Vinyl chloride ug/L |
|--------------|----------------|--------------|--------------|--------------------|---------------------|
| DMW-02       | 132            | 257          | 37.4         | 18.3               | 0.58                |

# Post-BiRD Pilot Test Injection at PRB2 Downgradient Plume

## 2/28/03 Data

| Monitor Well | 1,1,1-TCA ug/L | 1,1-DCA ug/L | 1,1-DCE ug/L | Chloro ethane ug/L | Vinyl chloride ug/L |
|--------------|----------------|--------------|--------------|--------------------|---------------------|
| GCTL         | 200            | 70           | 7            | 12                 | 1                   |
| NADC         | 2000           | 700          | 70           | 1200               | 100                 |
| IMW-30       | <1             | 750          | 82           | 1.1                | 110                 |

## 2015 Data

| Monitor Well | 1,1,1-TCA ug/L | 1,1-DCA ug/L | 1,1-DCE ug/L | Chloro ethane ug/L | Vinyl chloride ug/L |
|--------------|----------------|--------------|--------------|--------------------|---------------------|
| IMW-30       | 0.80 U         | 3.1          | 0.94 U       | 3.9                | 16                  |

# 2016 Data – 1,1-DCA concentration



# 2016 Data – 1,1-DCE concentration



# Summary and Conclusion

- Data suggests biogeochemical reduction (BiRD) is occurring, evidence of the formation of FeS particle in groundwater
- Source area well DMW-02 has significant increase in 1,1-DCA, which is a signature of biogeochemical reduction of 1,1,1-TCA
- Pyrite detected in soil samples analyzed by XRD – pre-injection, this provided an indication that biogeochemical reduction was already occurring.
- ... our job now was to enhance it.
- Post injection, soil samples analyzed by XRD detected iron and sulfur in the soil samples, further suggesting that biogeochemical reduction is occurring.
- Organic soils present at the source areas are sink for the COCs, and back diffusion of COCs are contributing to the groundwater plumes



# Lessons Learned

- Move quicker to remediation (took 3 years from assessment to remediation)
- Consider moving the former lab building (Rent temporary building on site for business and allow us to excavate source down to 30 feet)
- Perform vertical profiling sooner
- Consider outside in approach vs. inside out
- Perform MIP in initial stages of assessment
- More focused injection intervals, concerned with the delivery of the injectate
- Interesting to have performed a side by side pilot test comparing BiRD and biostimulation or bioaugmentation
- Results of BiRD are promising, very interesting
- geochemical signatures





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**Thank you!**

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