# Local Applications of Innovative Groundwater Cleanup Using Zero Valent Metals

January 31, 2008

***US EPA Region 9***

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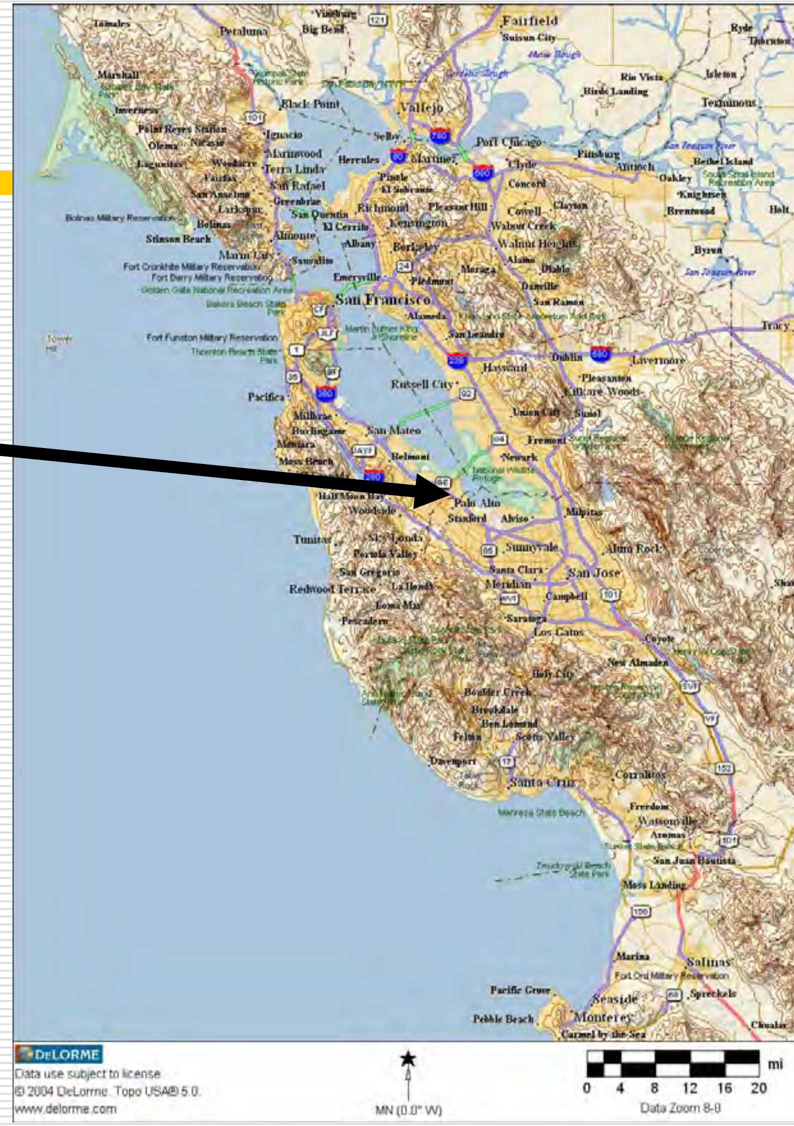
# OUTLINE

1. Site History and Conditions
2. Zero Valent Iron for GW Cleanup
3. Field Preparation and In Situ Testing of ZVI-Pd Nanoparticles in Palo Alto
4. Installation of a Multiple Funnel & Gate PRB in Palo Alto

SITE

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# PART 1: Site History and Conditions

i.e. What drove us to do this?

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# Site History – 20th Century

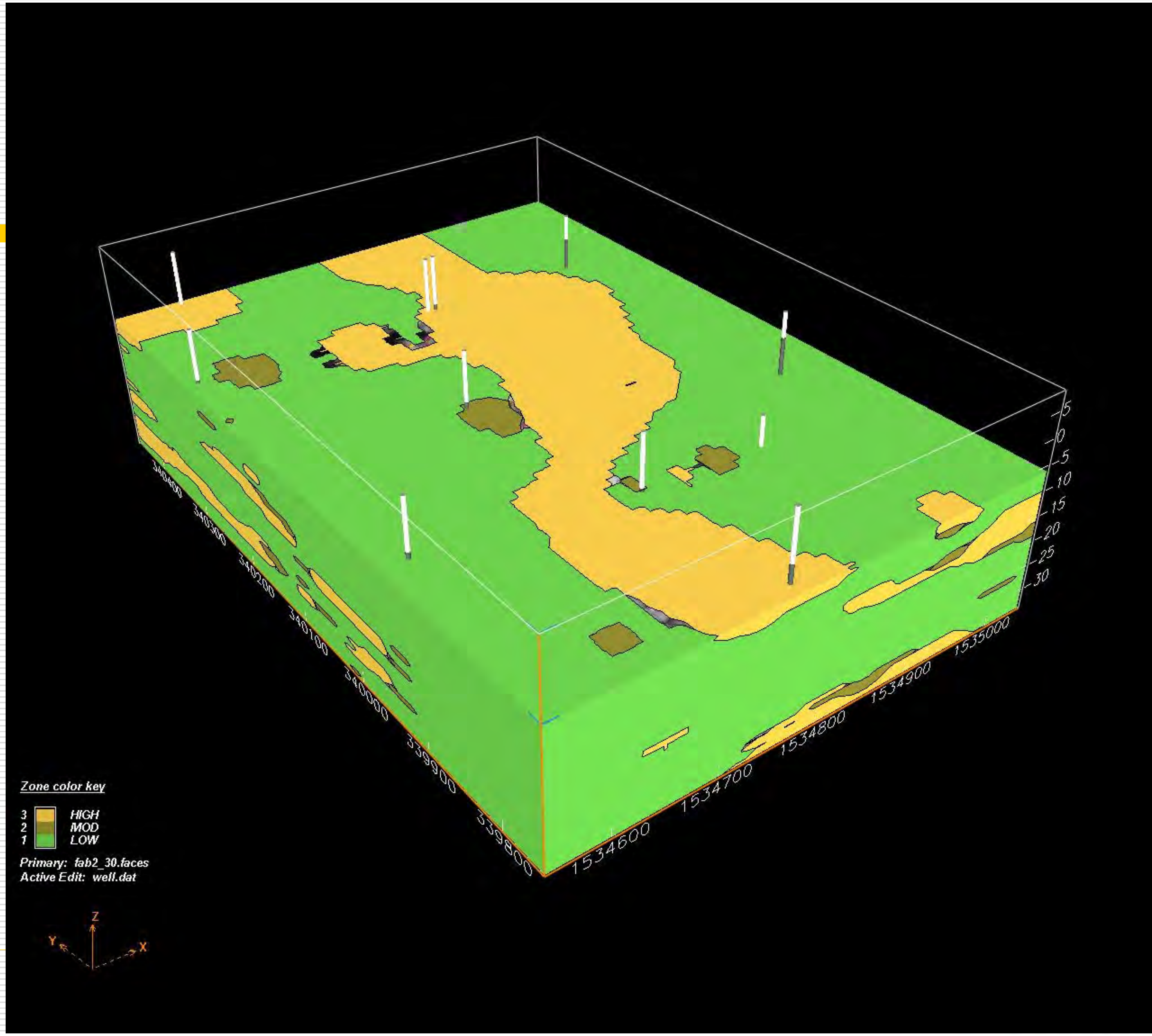
- Aerospace facility operated since the late 1950's
- Surface releases of PCE reportedly occurred along a fence line (weed control?)
- Characterization and GW Monitoring begins in the late 1980's (offsite plumes suspected)
- Soil remediation of source area in the mid-1990's (excavation of >5,000 cy with onsite thermal desorption)
- Dissolved plume contained by building dewatering sump, where discharge is treated and regulated under NPDES (as the IRM)
- Quarterly monitoring continues
- TCE plume arrives at upgradient monitoring well in the mid-90's

# Site History – 21st Century

- **2001** – Site is partitioned for redevelopment
- **2004** – GMX conducts first high-resolution investigation (>60 CPT locations, >140 GW samples); offsite plumes mapped, residual onsite source identified
- **2005** – GMX conducts high resolution source area characterization (MIP)
- **2006** – GMX pilot tests remediation technologies (ISB, ZVI, nZVI); Final GW Cleanup Plan submitted; completes "Transect G"
- **2007** – GMX Implements Cleanup Plan (PRB + ISB in the source area)

# Site Hydrogeology

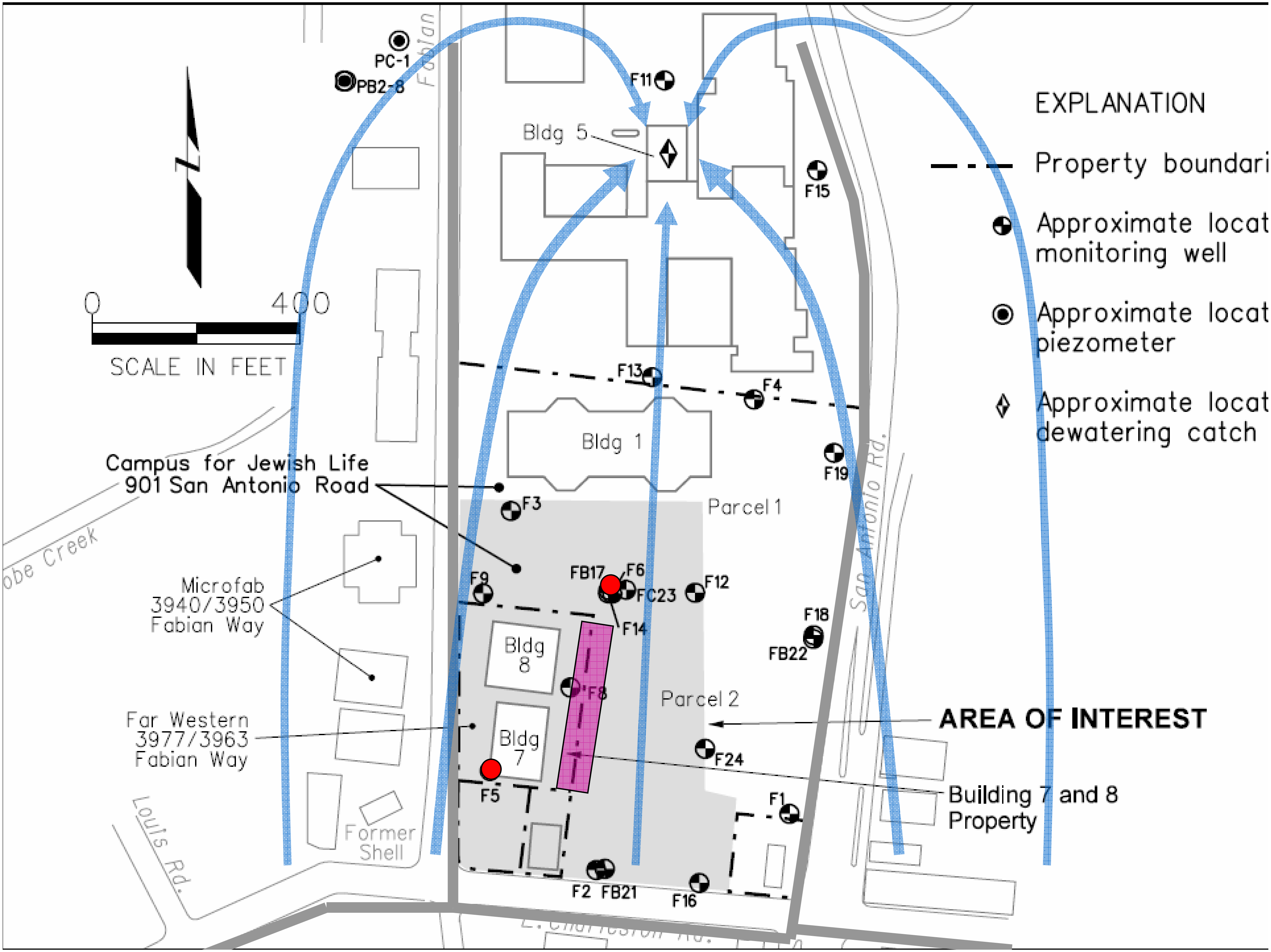
- Groundwater encountered at 8 to 10 feet below ground surface
- Water table at 6 feet below ground surface under confined conditions
- Complex alluvial environment
  - Multiple water-bearing units
  - sand and gravel zones separated by low-permeability clays
- Groundwater flow rates measured with tracer tests vary from 0.4 to 5.1 feet per day
- Groundwater flow direction and VOC migration controlled by ancient buried stream channels



Zone color key
3 HIGH
2 MOD
1 LOW
Primary: fab2_30.faces
Active Edit: well.dat
340400
340300
340200
340100
340000
339900
339800
1534600
1534700
1534800
1534900
1535000
5
10
15
20
25
30
Z
Y
X

# Chemical Distribution

- PCE in source zone up to 26,000 µg/L
- PCE in dissolved plume along northern property line at 850 µg/L from 10 - 60 ft bgs
- Offsite sources impact site, with TCE > 70,000 µg/L, Freon 113 > 1,000 µg/L

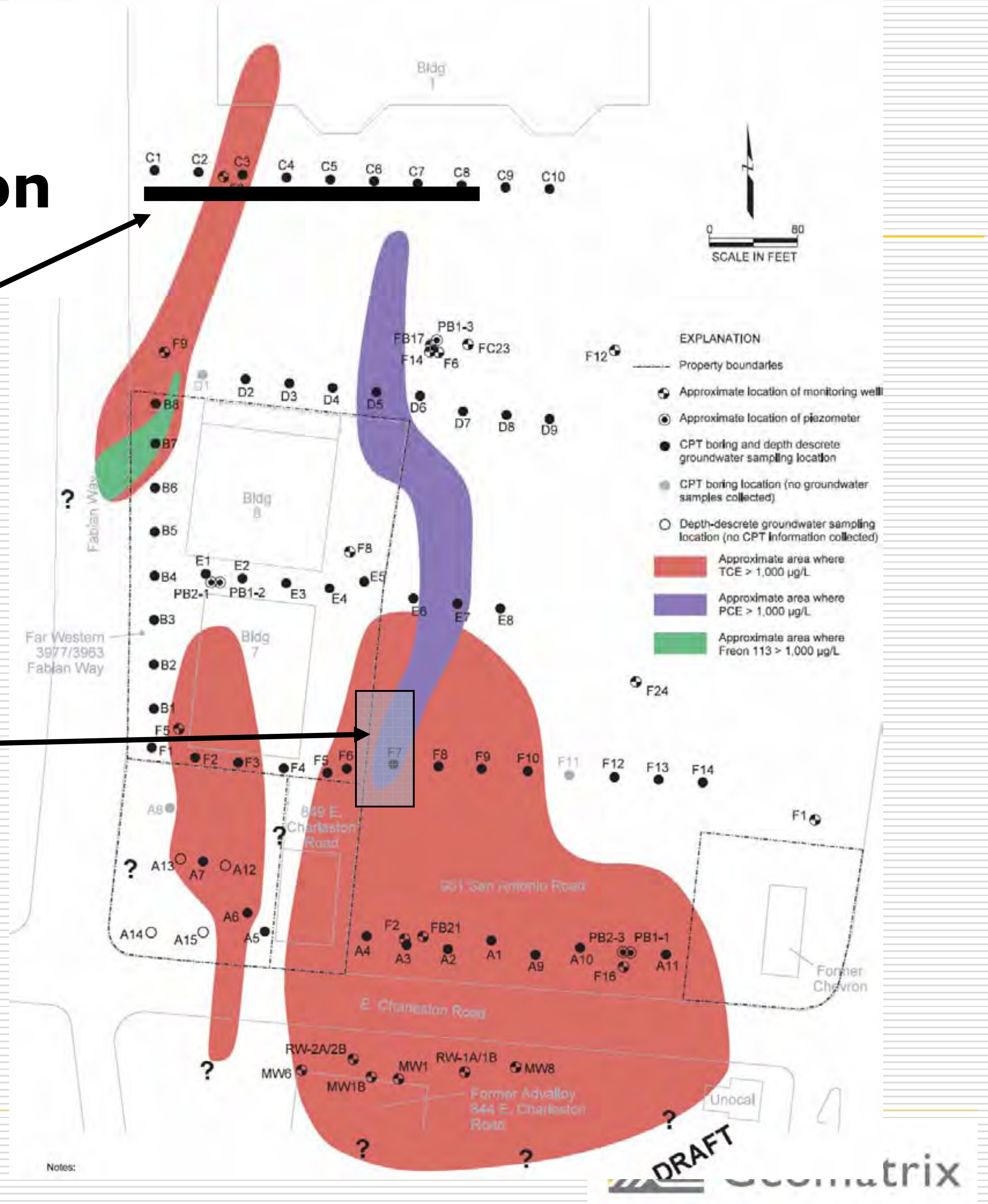


PC-1
PB2-8
Fabian
Bldg 5
F11
F15
EXPLANATION
Property boundari
Approximate locat
monitoring well
Approximate locat
piezometer
Approximate locat
dewatering catch
0
400
SCALE IN FEET
F13
F4
Bldg 1
F19
Campus for Jewish Life
901 San Antonio Road
F3
Parcel 1
obe Creek
Microfab
3940/3950
Fabian Way
F9
FB17
F6
FC23
F12
F14
F18
FB22
San Antonio Rd.
Bldg
8
F8
Parcel 2
AREA OF INTEREST
Far Western
3977/3963
Fabian Way
Bldg
7
F24
F5
F1
Building 7 and 8
Property
Louis Rd.
Former
Shell
F2
FB21
F16

# Characterization Results Drive Remediation Strategy

PRB

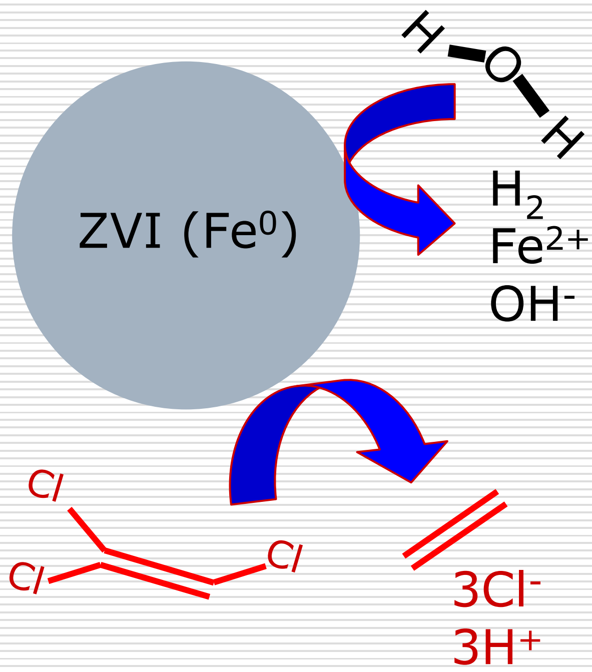
*in situ* source zone remediation



# PART 2: Treatment of Chlorinated VOCs with ZVI

A passive, low profile, low energy approach for chlorinated solvent sites.

# VOC Destruction on ZVI



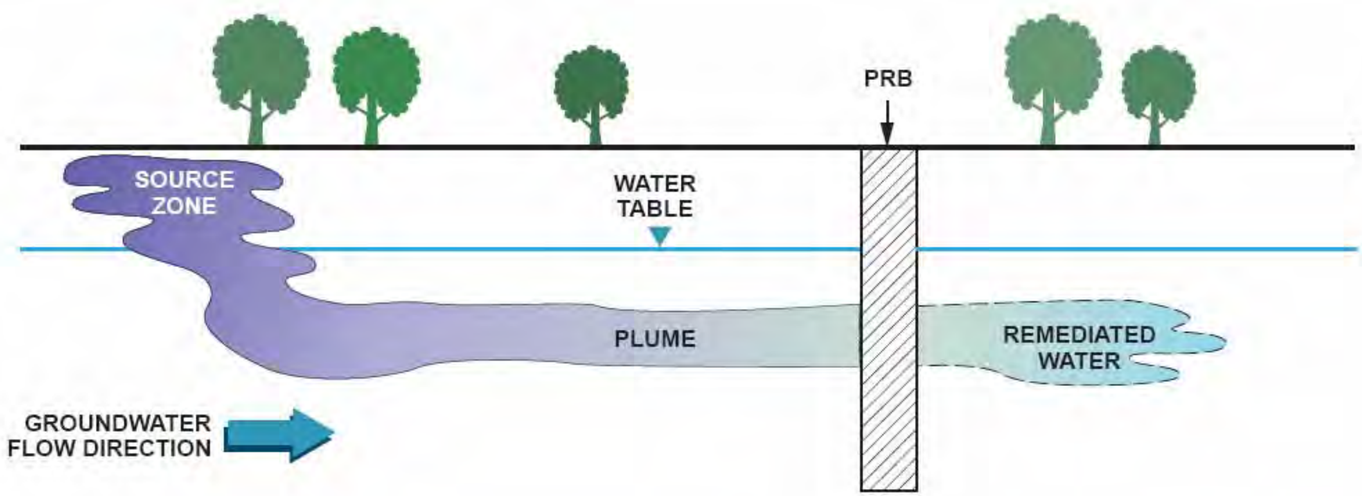

*ZVI: TCE half-life = 1 hour*

*nZVI: TCE half-life < 20 min*

**nZVI particles are coated with exotic metals such as palladium to catalyze destruction of contaminants such as TCE*

# PRB composed of ZVI:

- Dissolved plume containment with a permeable reactive barrier (PRB)

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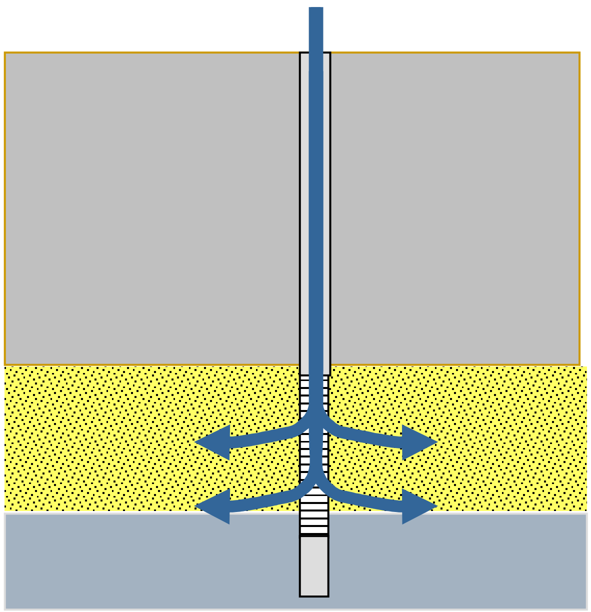
# Metallic Nanoparticles for Groundwater Cleanup

- 1 to 100 nanometers in diameter
- Usually formed by precipitation from metallic ions
- Small = fast reaction rates (good catalysts)
- Small = effective delivery to natural systems

# Source Treatment with nZVI:

- nZVI particles are injected into a well and transported through the source area by advection



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# Big Picture Questions on metallic nanoparticles (nZVI)

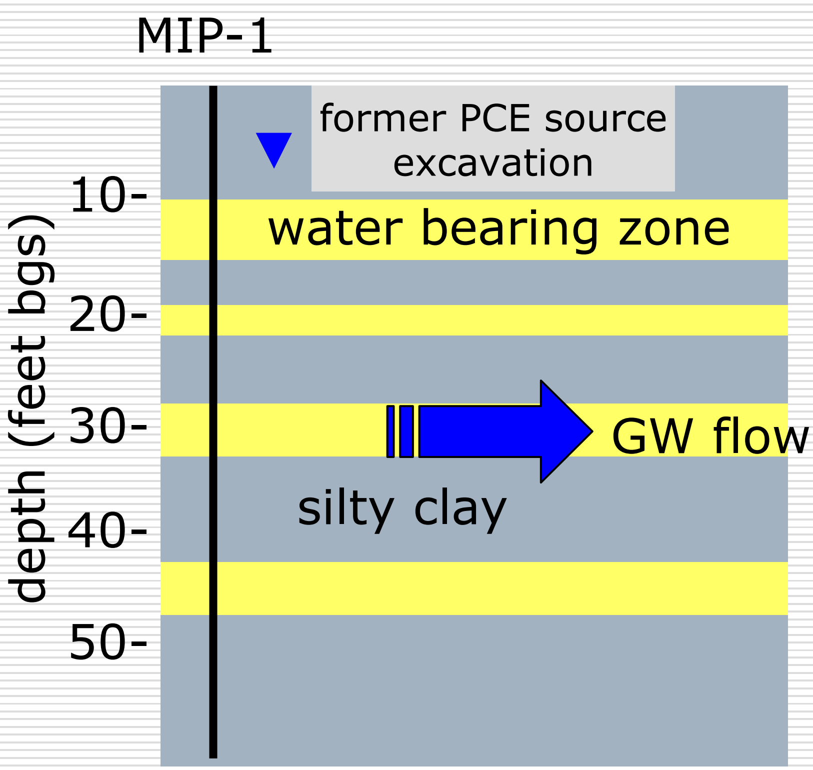
1. Delivery?
2. Reactive Lifetime?
3. Dose (i.e. suspension concentration)?
4. Cost of Cleanup?

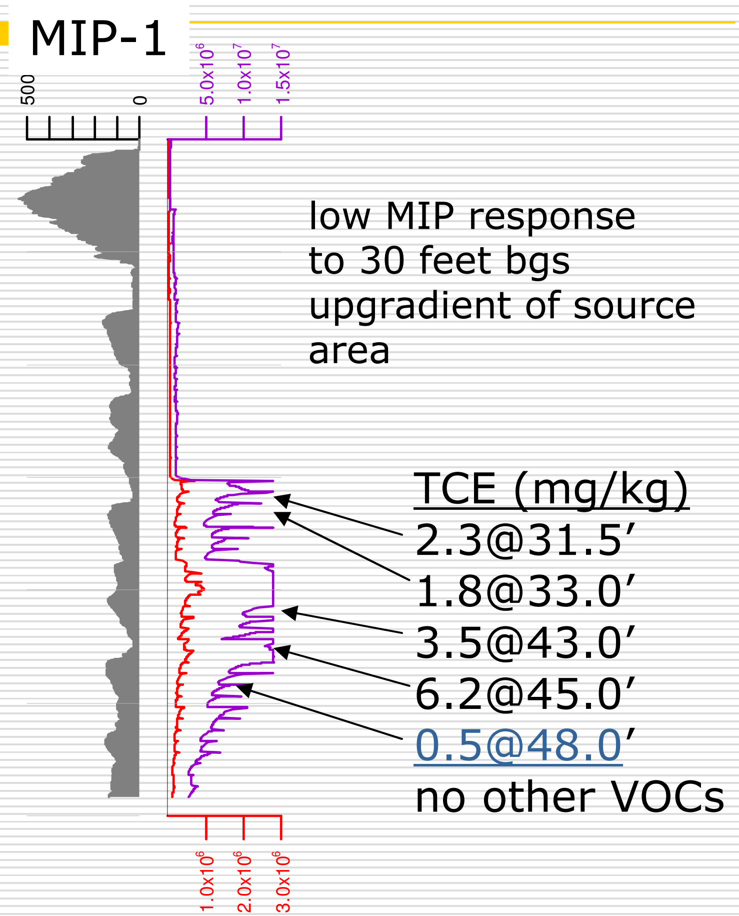
- *Assuming $50 per pound, 1 g Fe/L, cost for treating 1 cy = $21 (materials costs only)*

# PART 3: Onsite Preparation and Field Testing of Reactive Metal Nanoparticles

Fun with exotic chemicals…

# Source Area: Upgradient Plume




This MIP profile indicated the location of an offsite TCE plume

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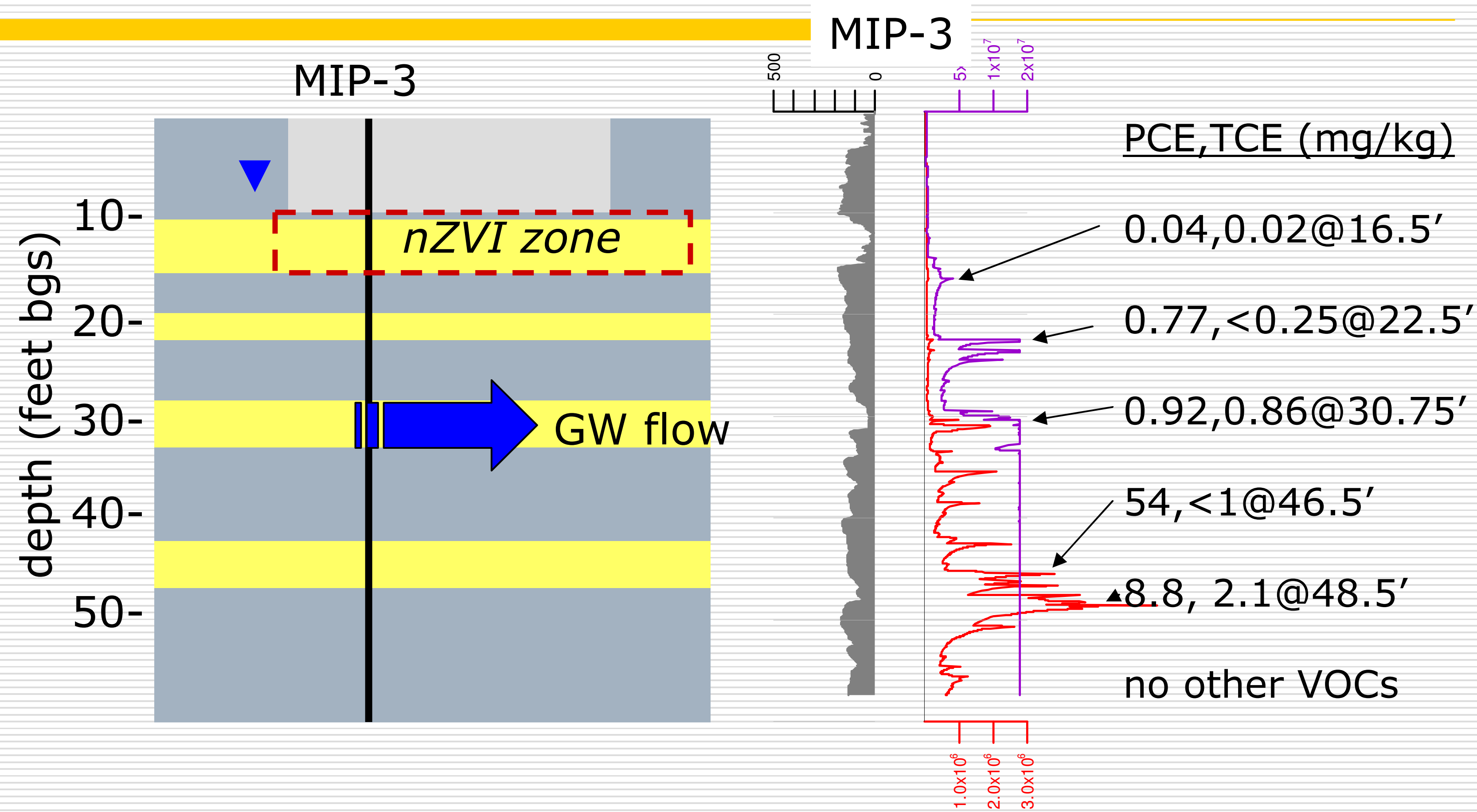
# Source Area: Commingled Release

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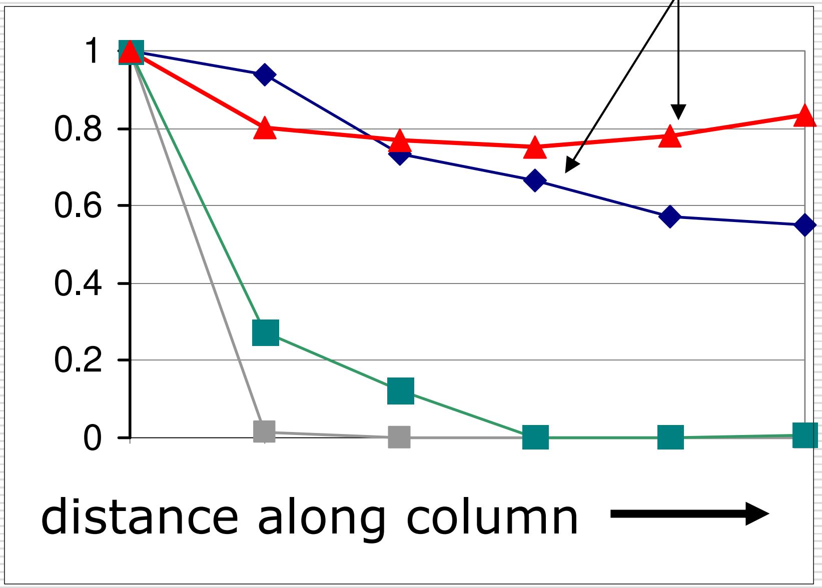
# Nano-Scale Iron Column Tests


"starch-stabilized" nano iron

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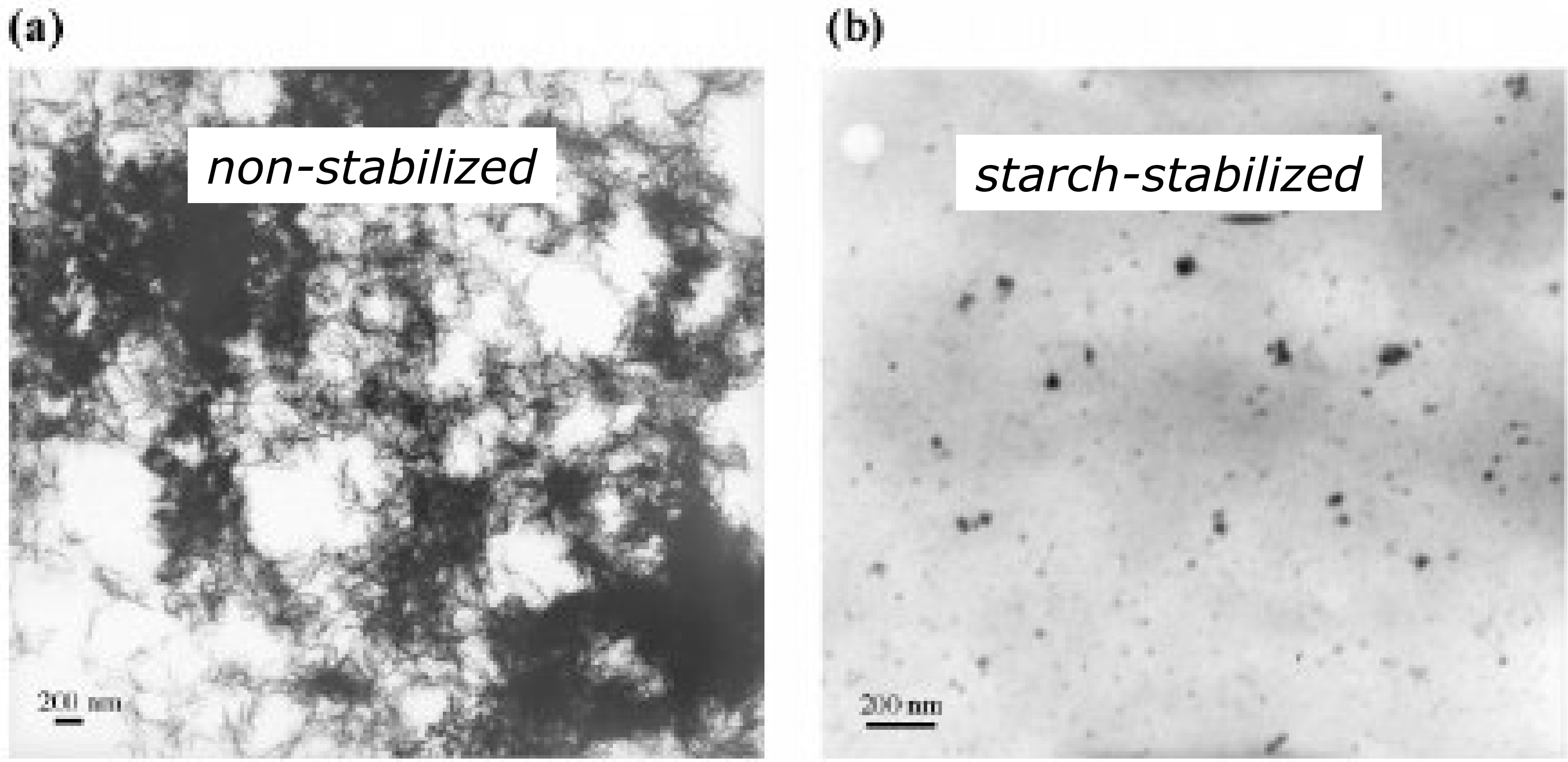
# Starch-Stabilized nZVI Particles




**Feng He and Dongye Zhao, 2005**. Preparation and Characterization of a New Class of Starch-Stabilized Bimetallic Nanoparticles for Degradation of Chlorinated Hydrocarbons in Water, *Environ. Sci. Technol*., 39, 3314-3320.

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# Our Specific Objectives

- Prepare "starch-stabilized" nZVI particles in suspensions of sufficient volume for field testing
- Assess *in situ* transport and reactivity of nZVI particles by a series of Push-Pull Tests

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# Synthesis of nZVI:

1. Prepare Starch (CMC 90K) and Ferrous Iron solution (remove $O_2$)

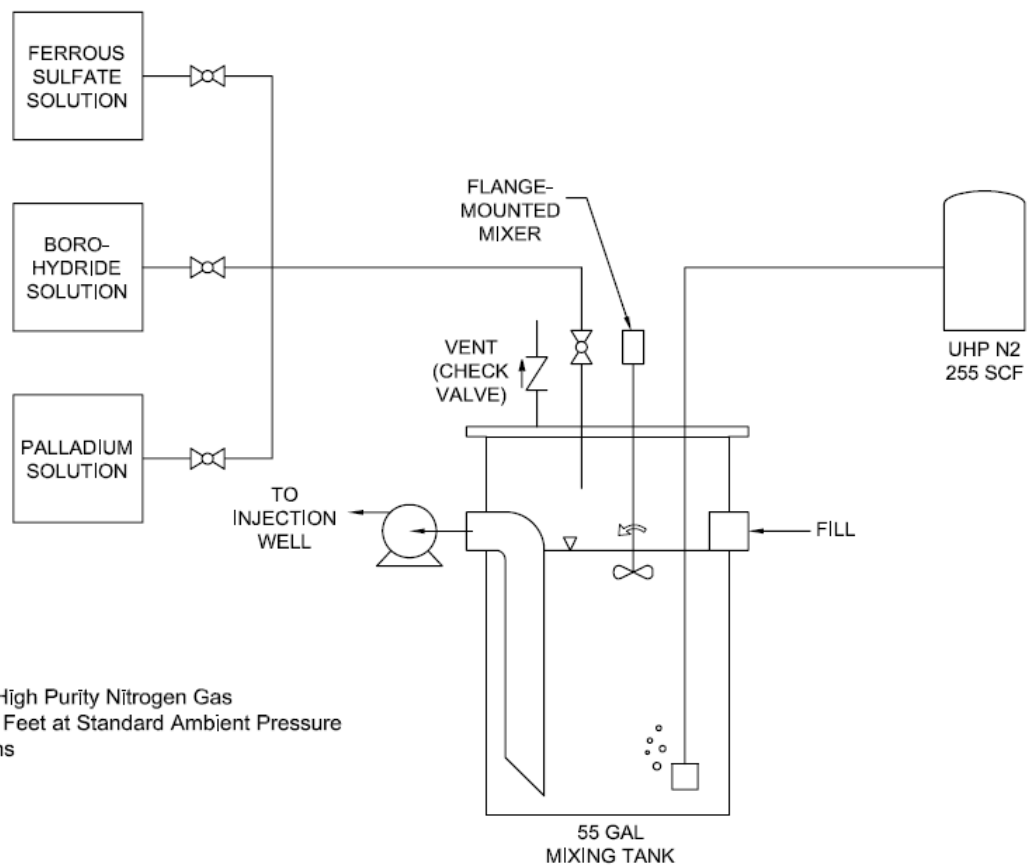
2. Reduce Ferrous Iron with Borohydride

$$Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow Fe^0 + 7H_2 + 2B(OH)_3$$

3. Coat nZVI particles with Palladium Metal

$$Pd^{4+} + Fe^0 \rightarrow Pd^0 + Fe^{2+}$$

# 3. Field Batch Reactor




NOTES:

| | | |
|---|---|---|
| UHP N2 | = | Ultra High Purity Nitrogen Gas |
| SCF | = | Cubic Feet at Standard Ambient Pressure |
| GAL | = | Gallons |

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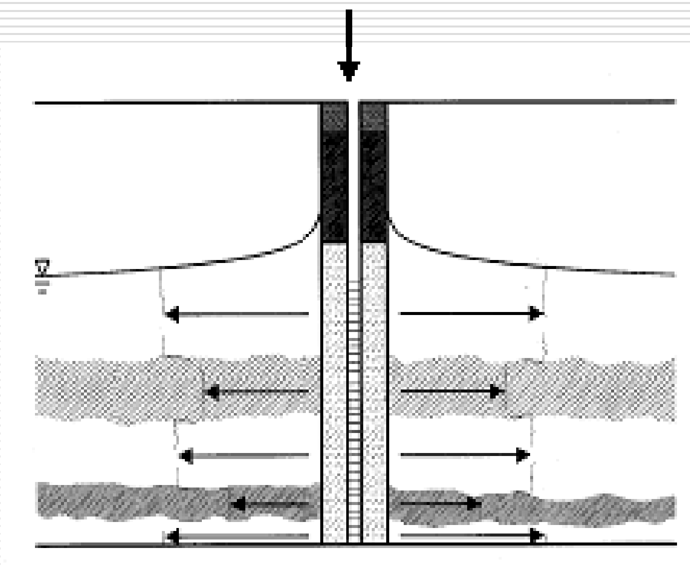
# Summary of nZVI batches

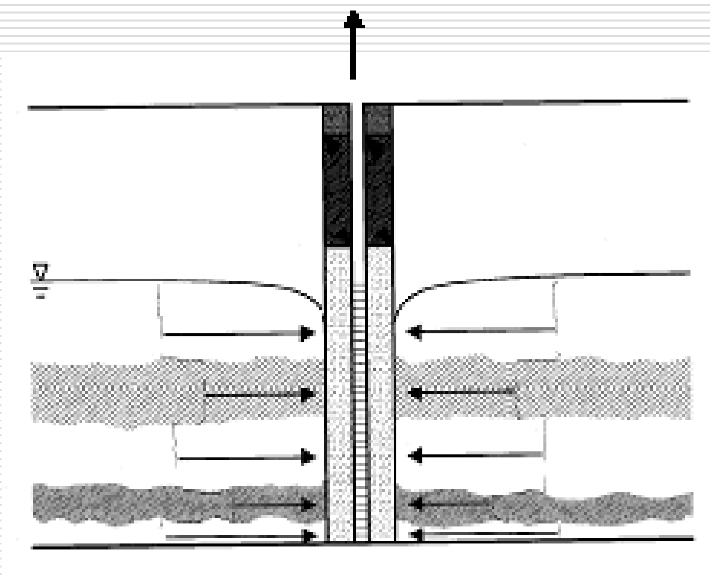
| Reagent | Units | Test Batches | | |
|---|---|---|---|---|
| | | PPT-2 | PPT-3 | PPT-4 |
| Volume | L | 117 | 113 | 329 |
| Starch - NaCMC (90K) | Wt% | 0.82 | 0.40 | 0.29 |
| Iron | mg/L | 962 | 207 | 345 |
| Borohydride (as B) | mg/L | 371 | 80 | 136 |
| Palladium (as Pd) | mg/L | 0 | 0 | 0.329 |
| Sodium Bromide – as Br | mg/L | 285 | 284 | 140 |

# Push-Pull Tests

PUSH



PULL



FIGURES FROM OREGON STATE UNIVERSITY WEBSITE.

# Injection Wellhead

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# Push-Pull Tests

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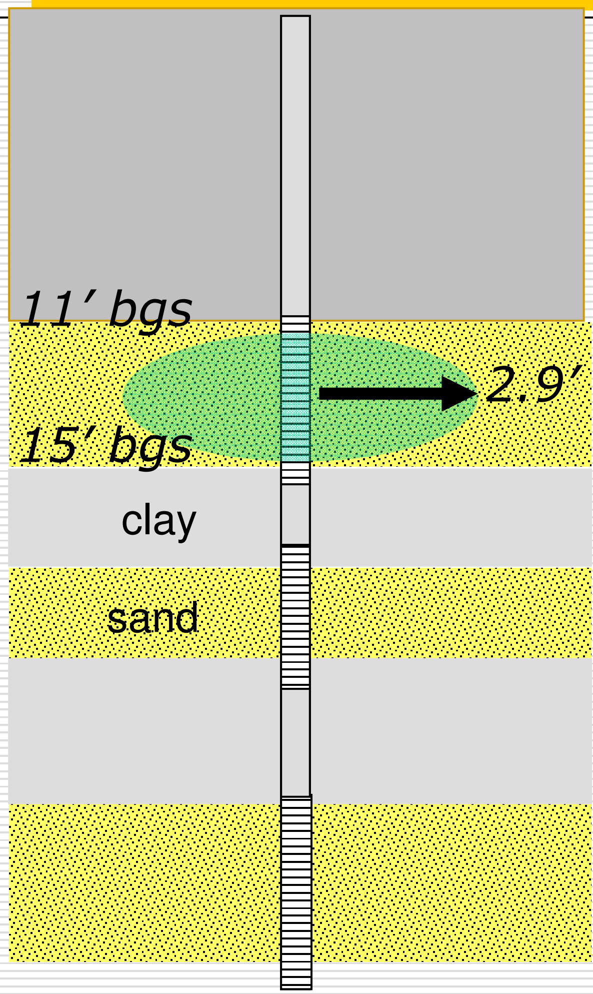
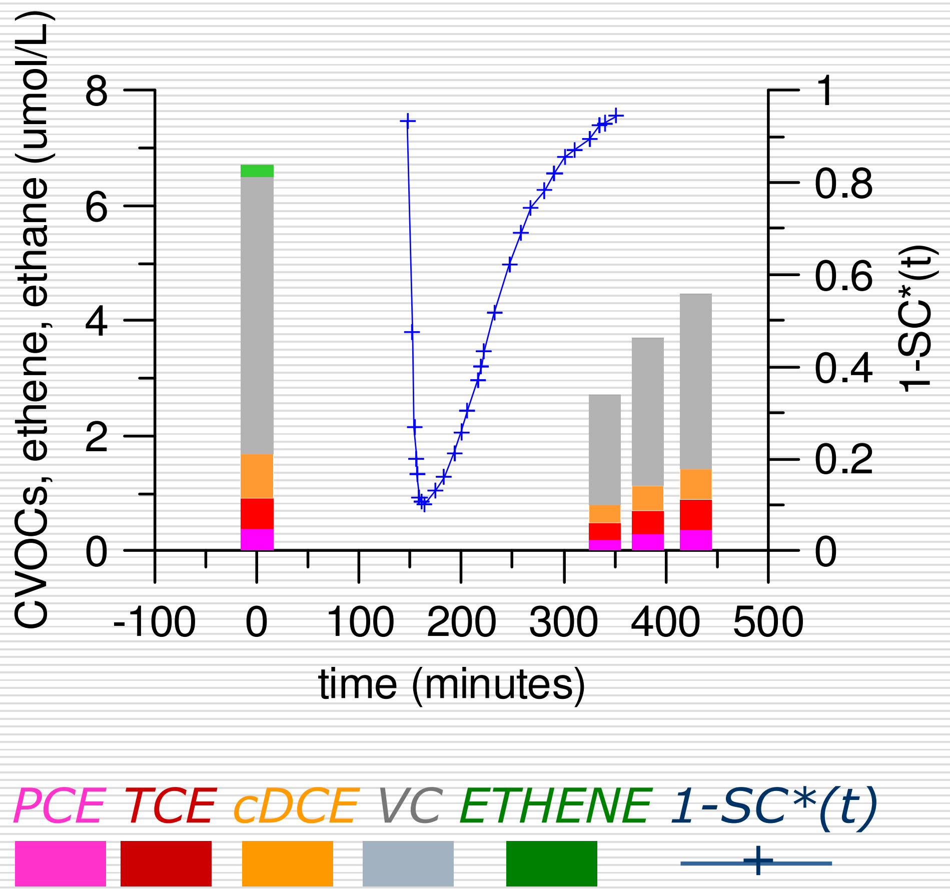
$V_{inj}$ = 699+53 L, $V_{ext}$ = 1,440 L, $V_{ext}/V_{inj}$=1.9

# Push-Pull Test #1

## Tap Water Injection

$$SC^*(t) = \frac{SC_t - SC_{gw}}{SC_{inj} - SC_{gw}}$$

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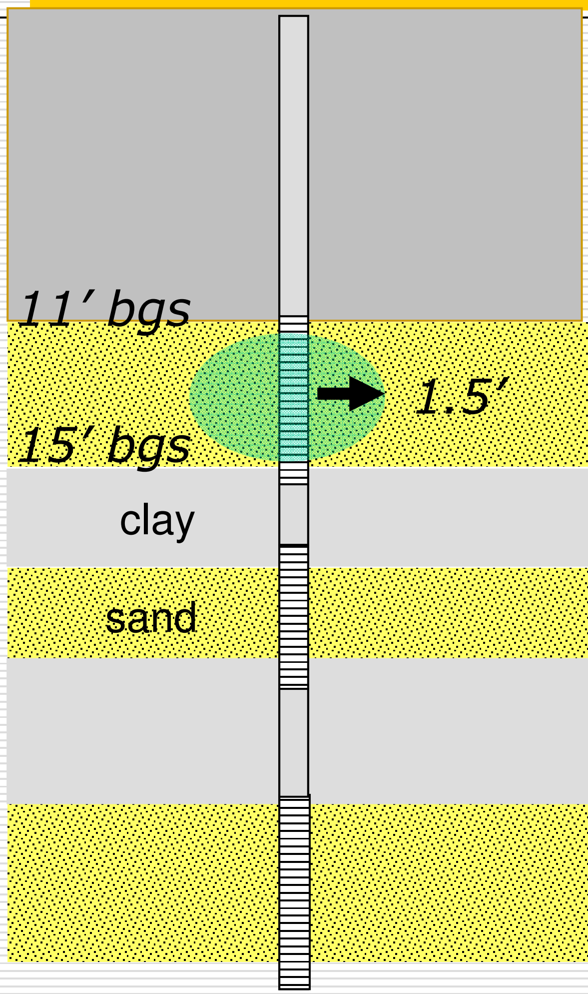
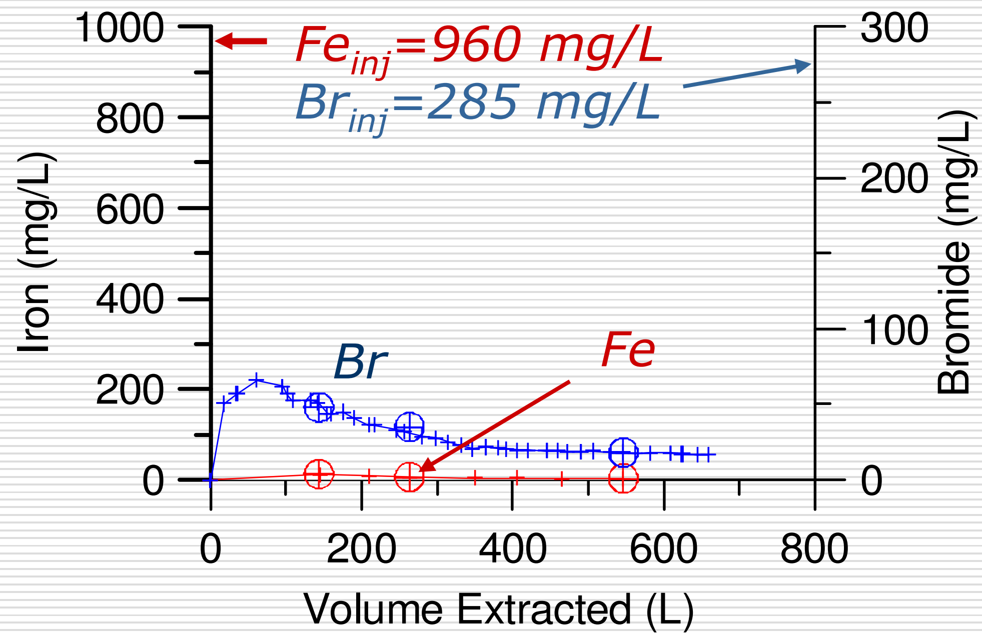
# Push-Pull Test #2

## nZVI (960 mg/L), 13 hr between injection & extraction



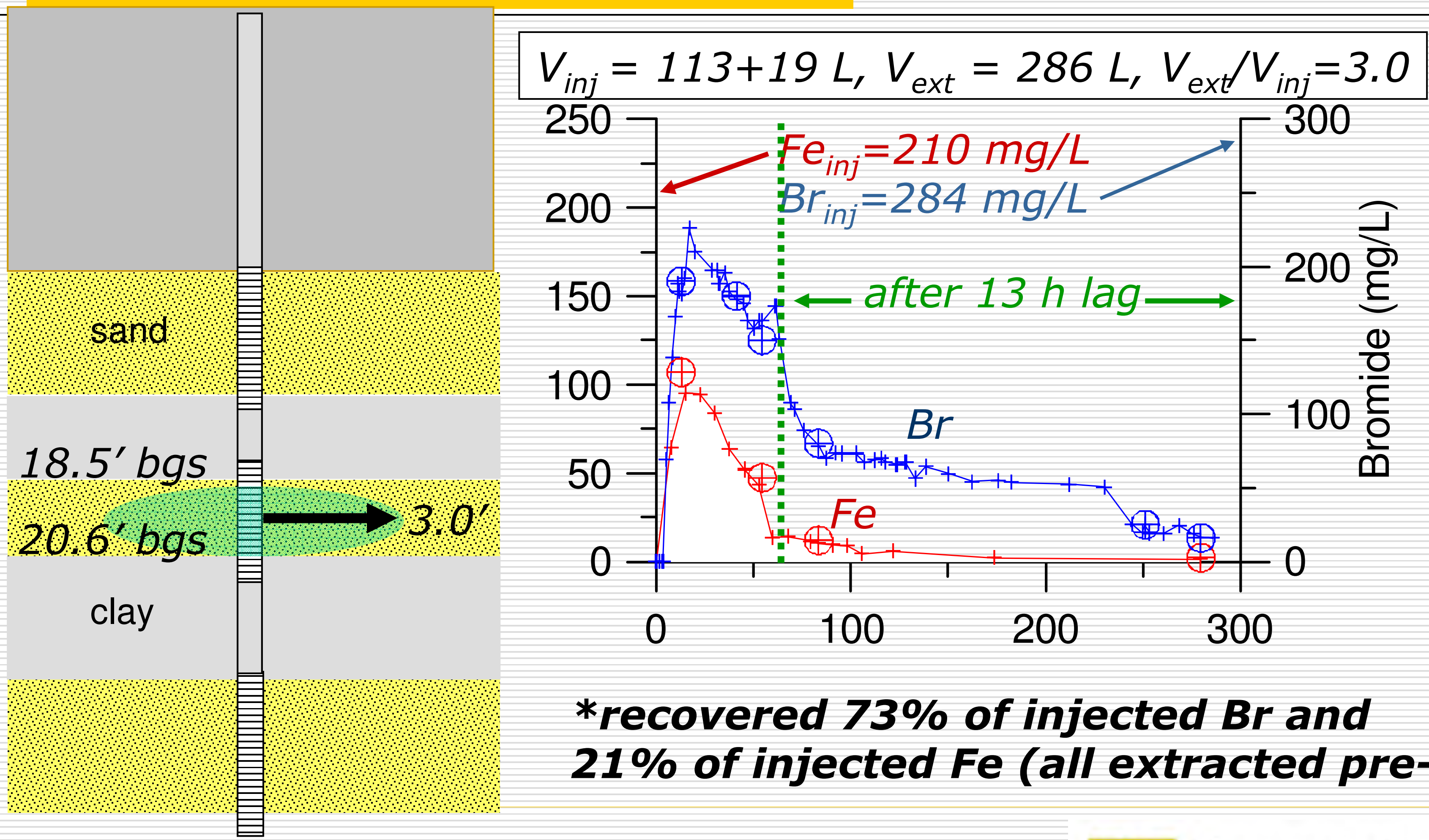

$V_{inj}$ = 117+111 L, $V_{ext}$ = 659 L, $V_{ext}/V_{inj}$=2.9




***recovered 61% of injected Br, but only 2.6% of injected Fe**

# Push-Pull Test #3

## nZVI (210 mg/L), 13 hr lag after extracting 60 L




***recovered 73% of injected Br and 21% of injected Fe (all extracted pre-lag)**

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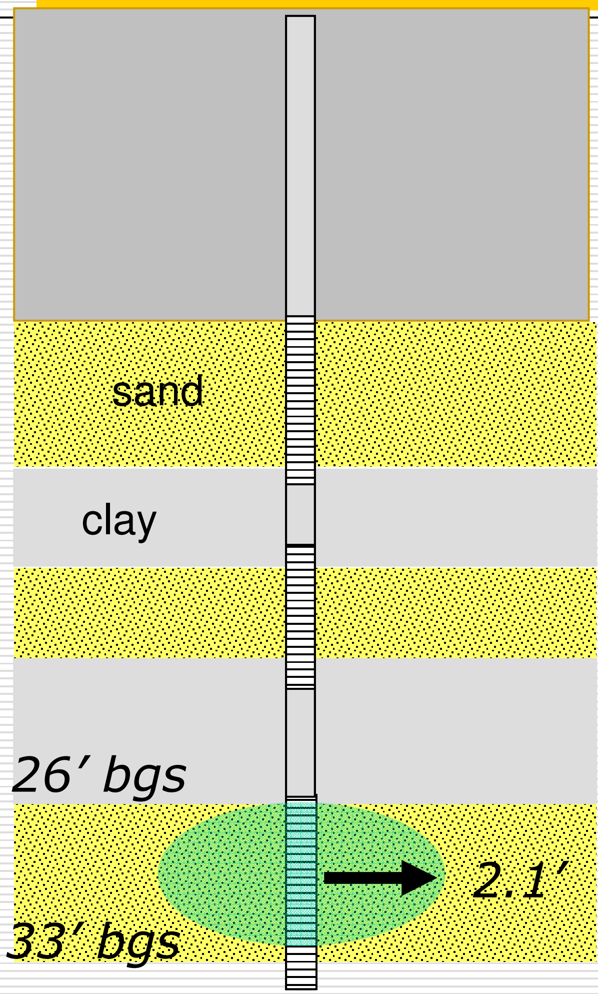
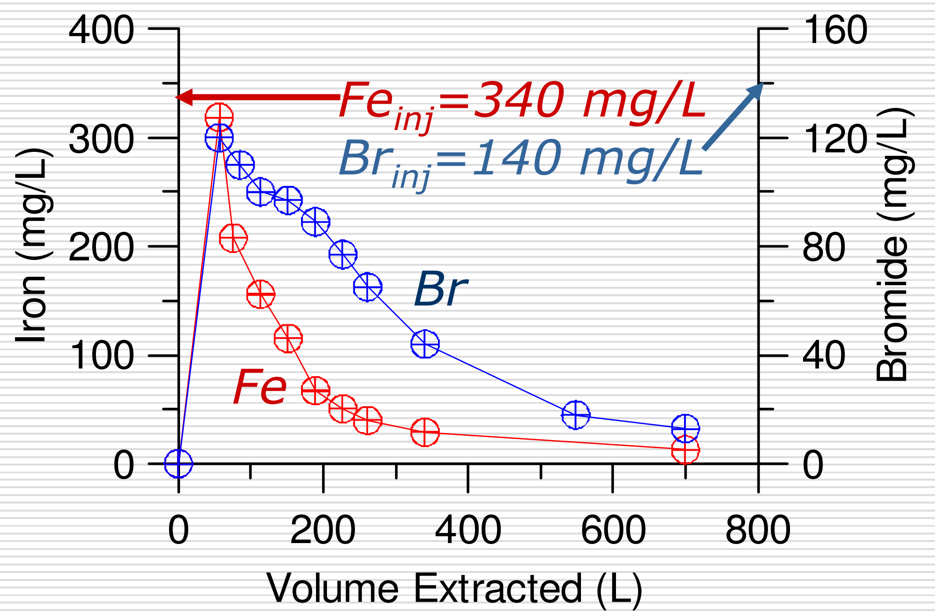
# Push-Pull Test #4

## nZVI (340 mg/L),no lag time




$V_{inj}$ = 329+40 L, $V_{ext}$ = 756 L, $V_{ext}/V_{inj}$=2.0




***recovered 76% of injected Br and 31% of injected Fe (best recovery of 3 PP tests)**

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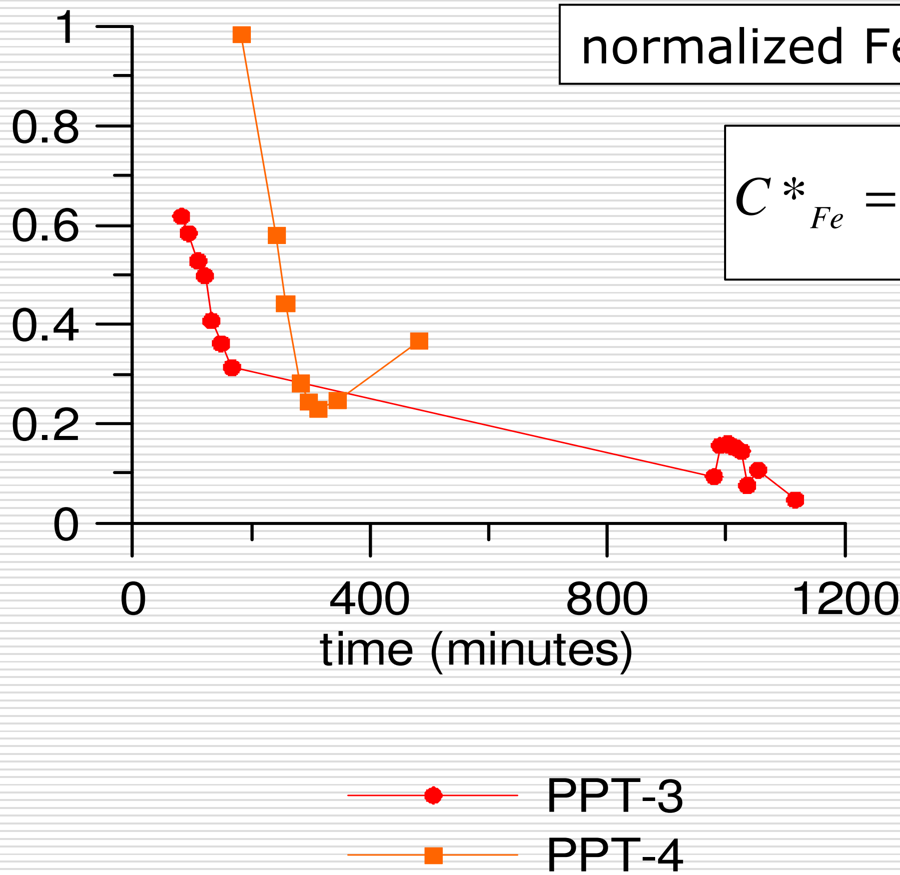
# Push-Pull Tests #3 & #4

## Decrease in iron mobility with time




normalized Fe concentration = $C^*_{Fe}/C^*_{Br}$

$$C^*_{Fe} = \frac{Fe(t)}{Fe(inj)}$$

$$C^*_{Br} = \frac{Br(t)}{Br(inj)}$$

*The decrease in normalized Fe concentration to <0.5 within 200 – 300 minutes suggests that nZVI mobility is significantly reduced within hours of injection.*

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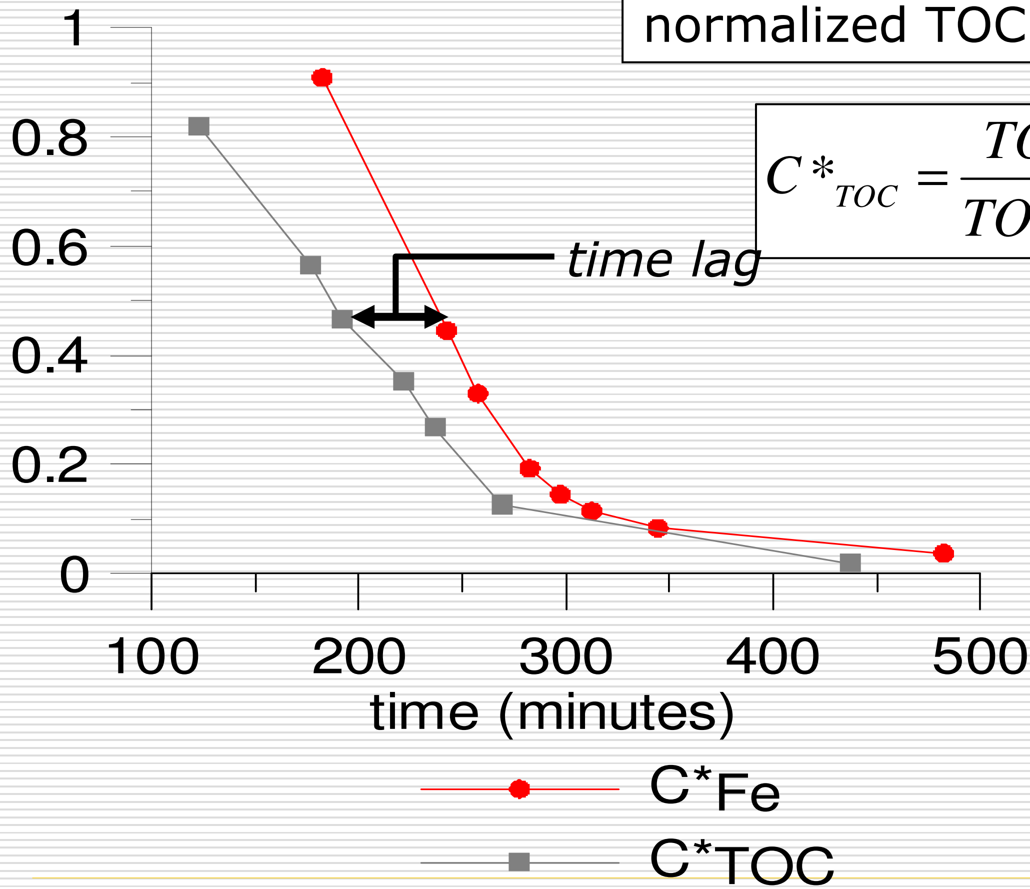
# Push-Pull Test#4

## Starch degradation as a potential explanation for loss of nZVI mobility




normalized TOC concentration = $C^*_{TOC}/C^*_{Br}$

$$C^*_{TOC} = \frac{TOC(t)}{TOC(inj)}$$

$$C^*_{Br} = \frac{Br(t)}{Br(inj)}$$

*C*TOC decrease suggests it is being mineralized in situ. Time lag between C*TOC decrease and C*Fe decrease suggests that nZVI may lose mobility due to consumption of starch.*

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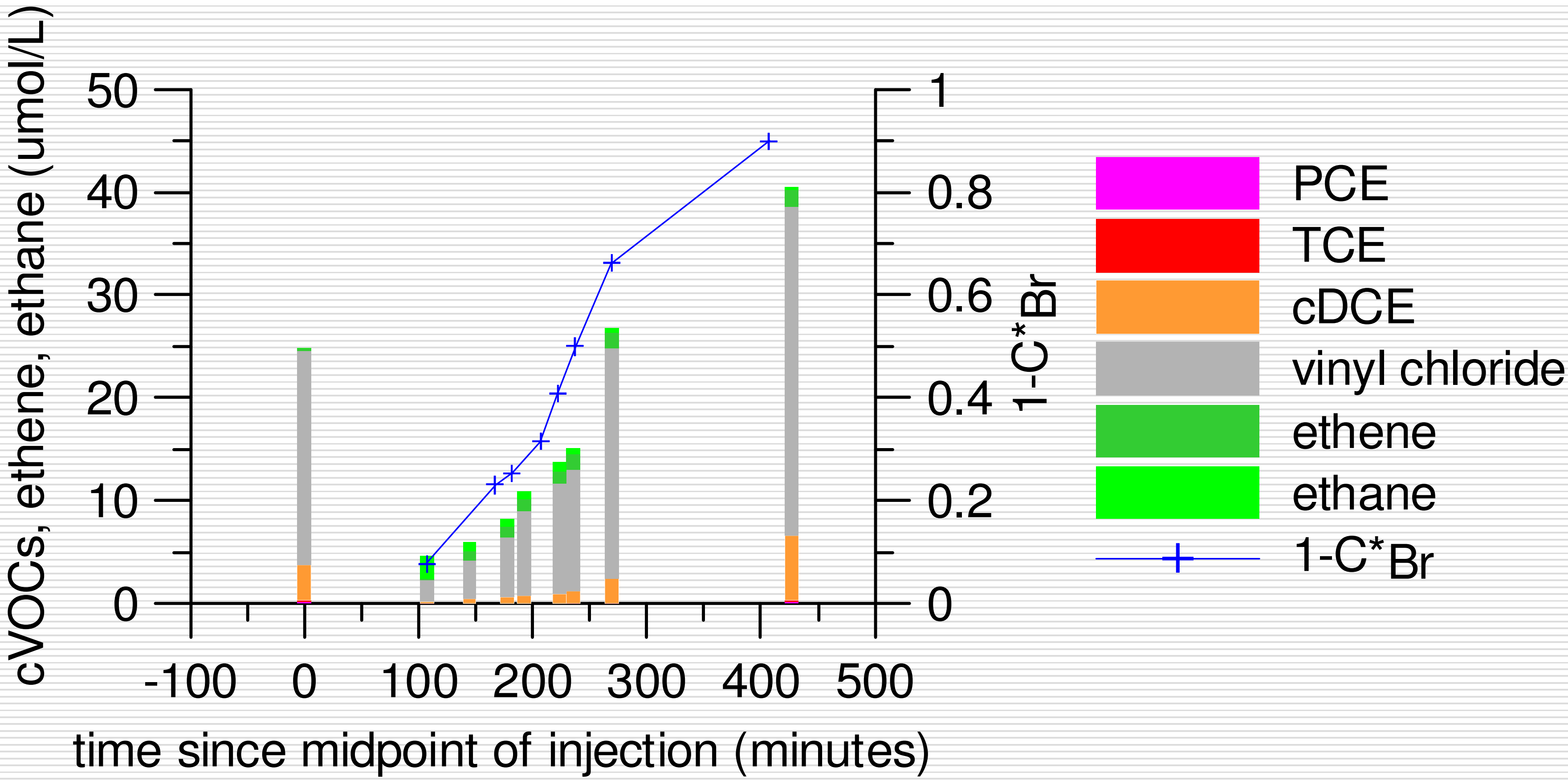
# Push-Pull Test #4

## Reactivity Assessment

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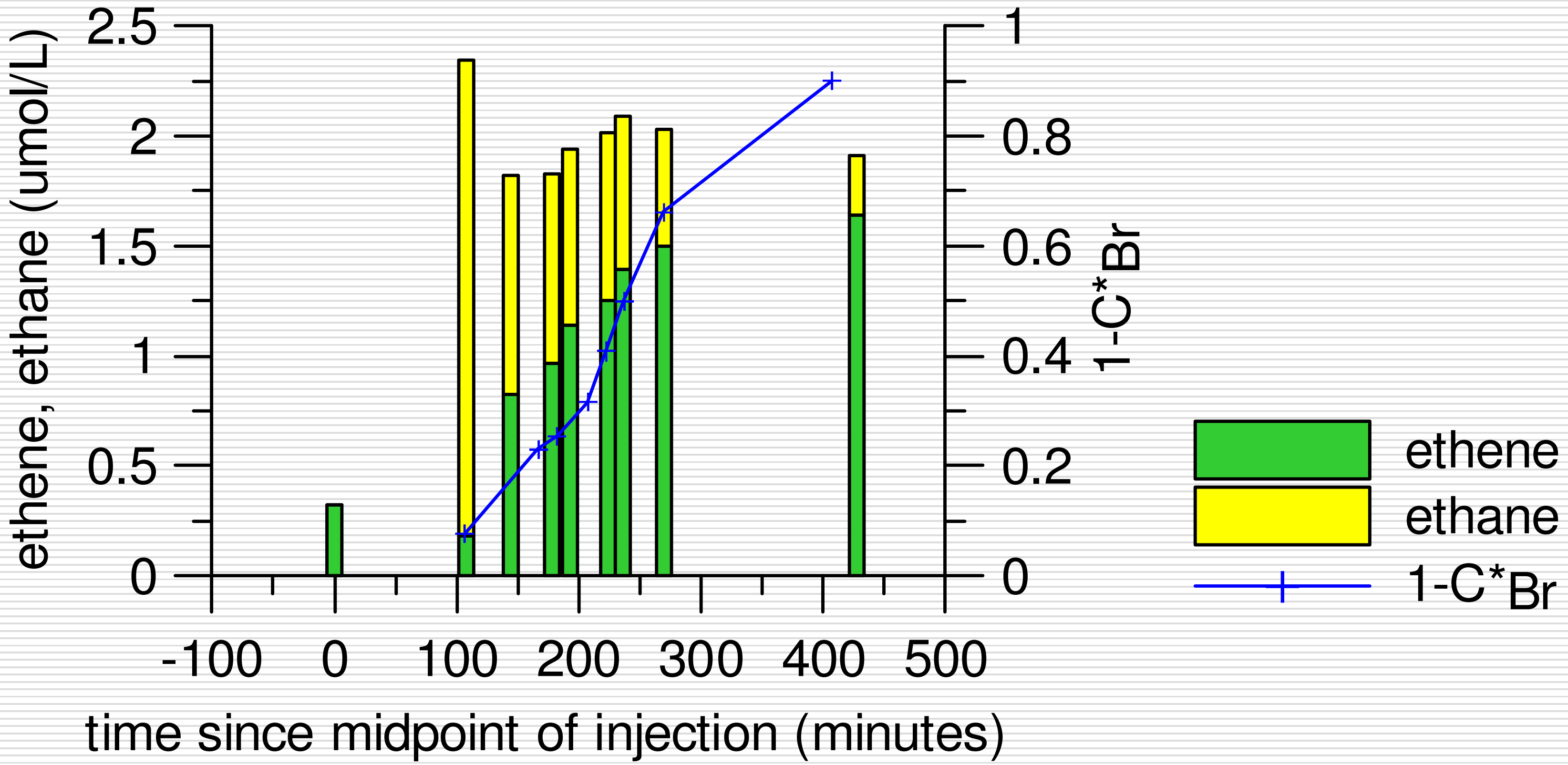
# Push-Pull Test #4
## Ethane and Ethene Production

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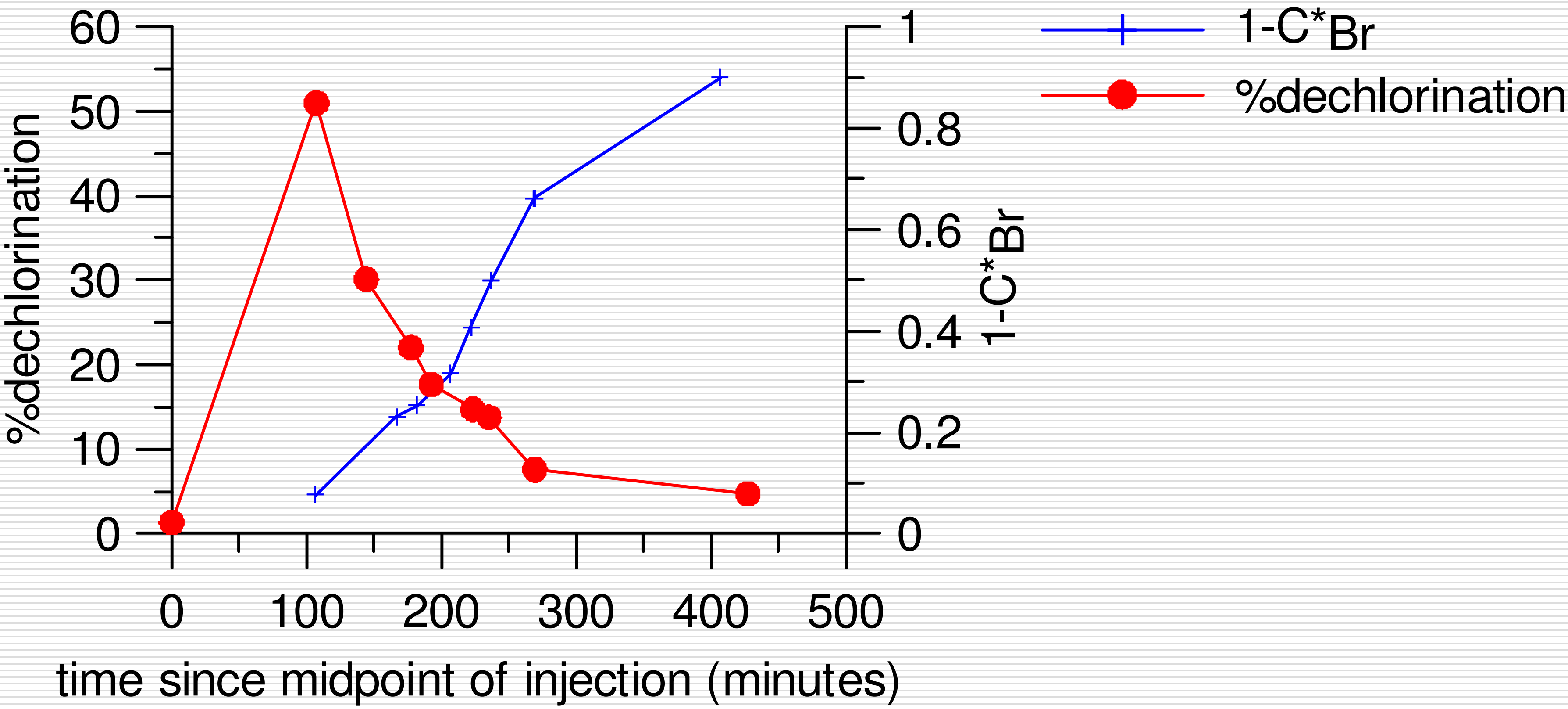
# Push-Pull Test #4

## %Dechlorination of CVOCs in extracted water samples




$$\%dechlorination = \frac{[ethene]+[ethane]}{[PCE]+[TCE]+[cDCE]+[VC]+[ethene]+[ethane]} \times 100\%$$

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# Conclusions

- Field preparation of nanoparticles is feasible
- Mobility is short-lived, perhaps because the stabilizer is consumed quickly in the subsurface
- Complete dechlorination of CVOCs occurred at a rapid rate
- More information is needed to scale-up nZVI applications to full scale

# PART 4: Installation of a Multiple Funnel&Gate PRB

The design was based on a very high resolution transect of lithology and gw chemistry

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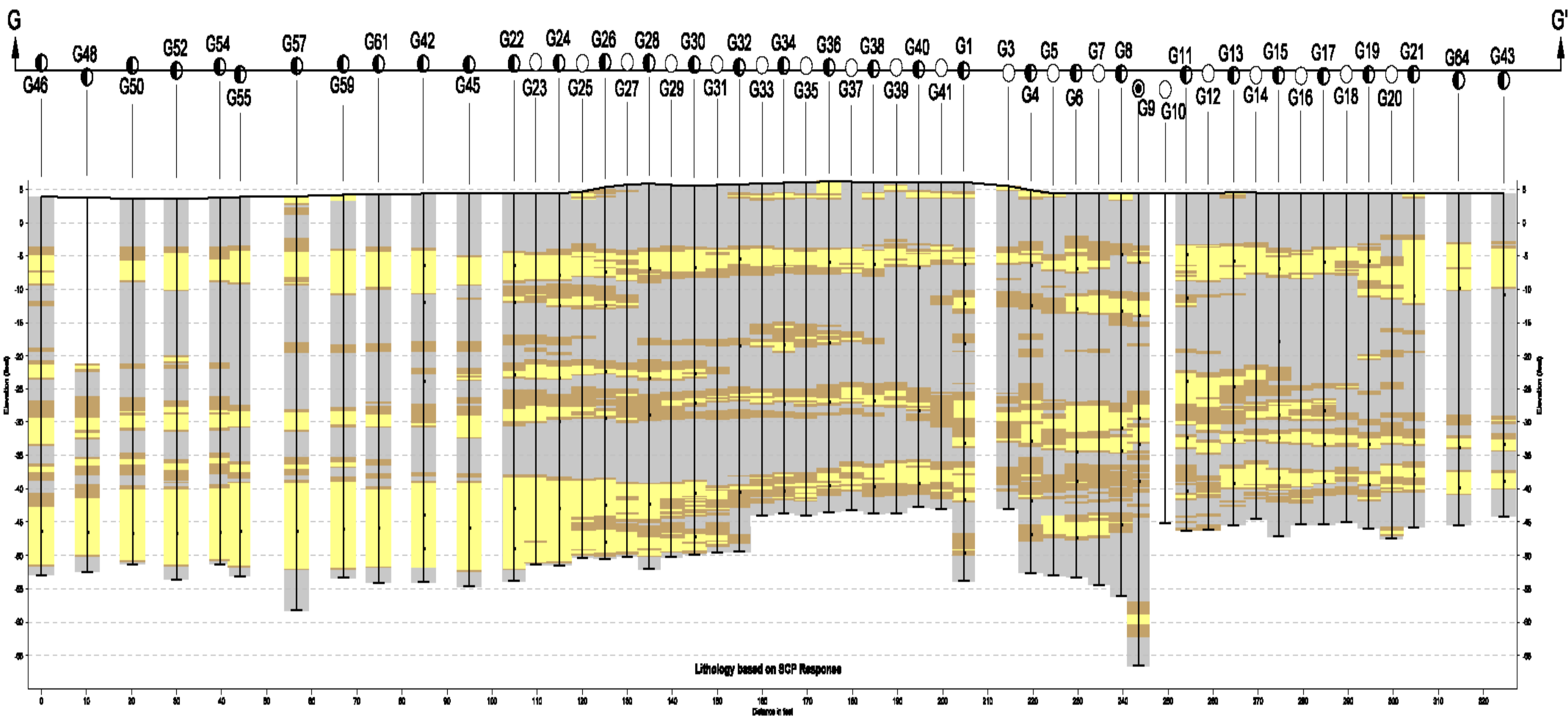
# Cross-section Along Northern Property Boundary

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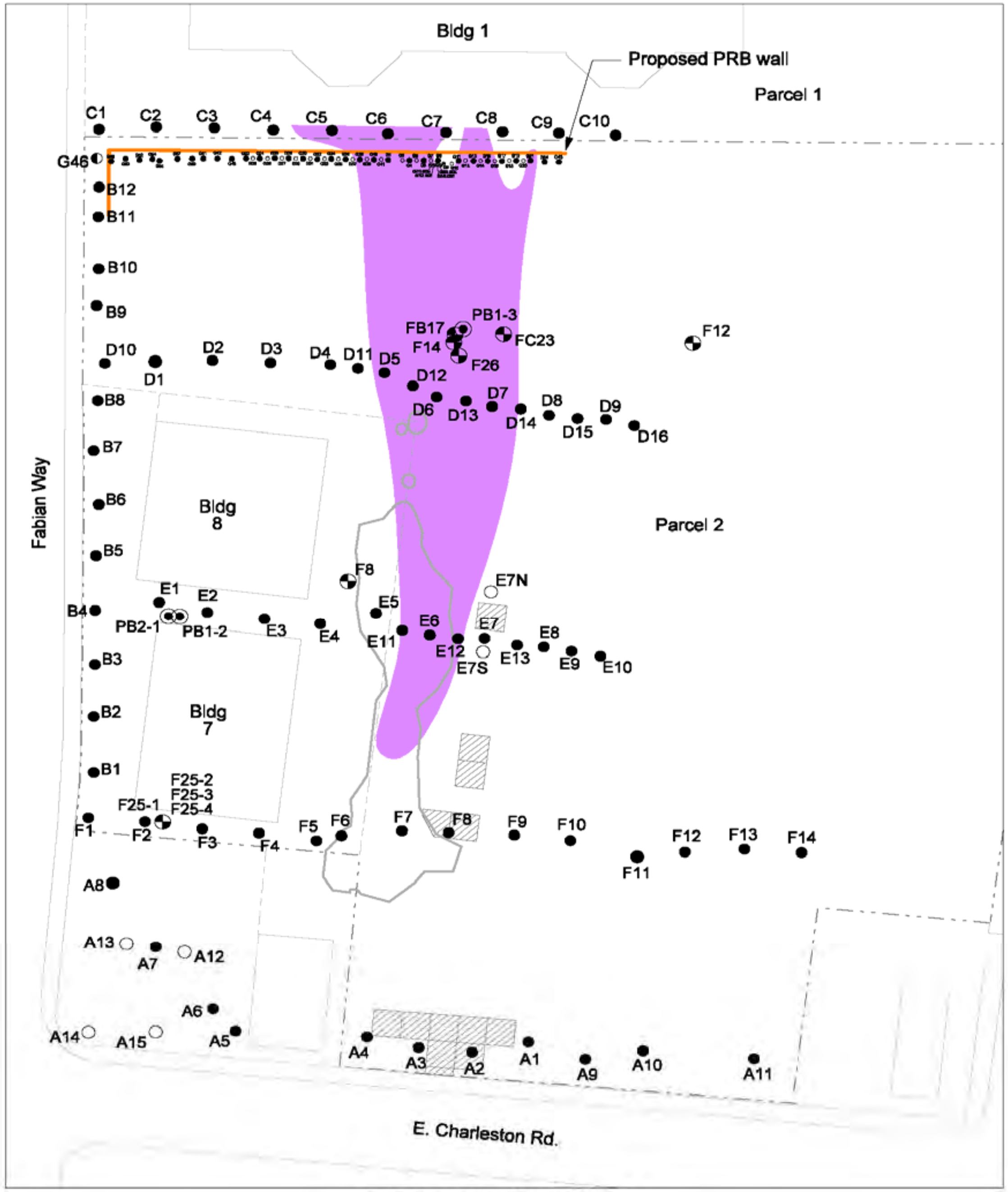
# PCE > 100 ppb

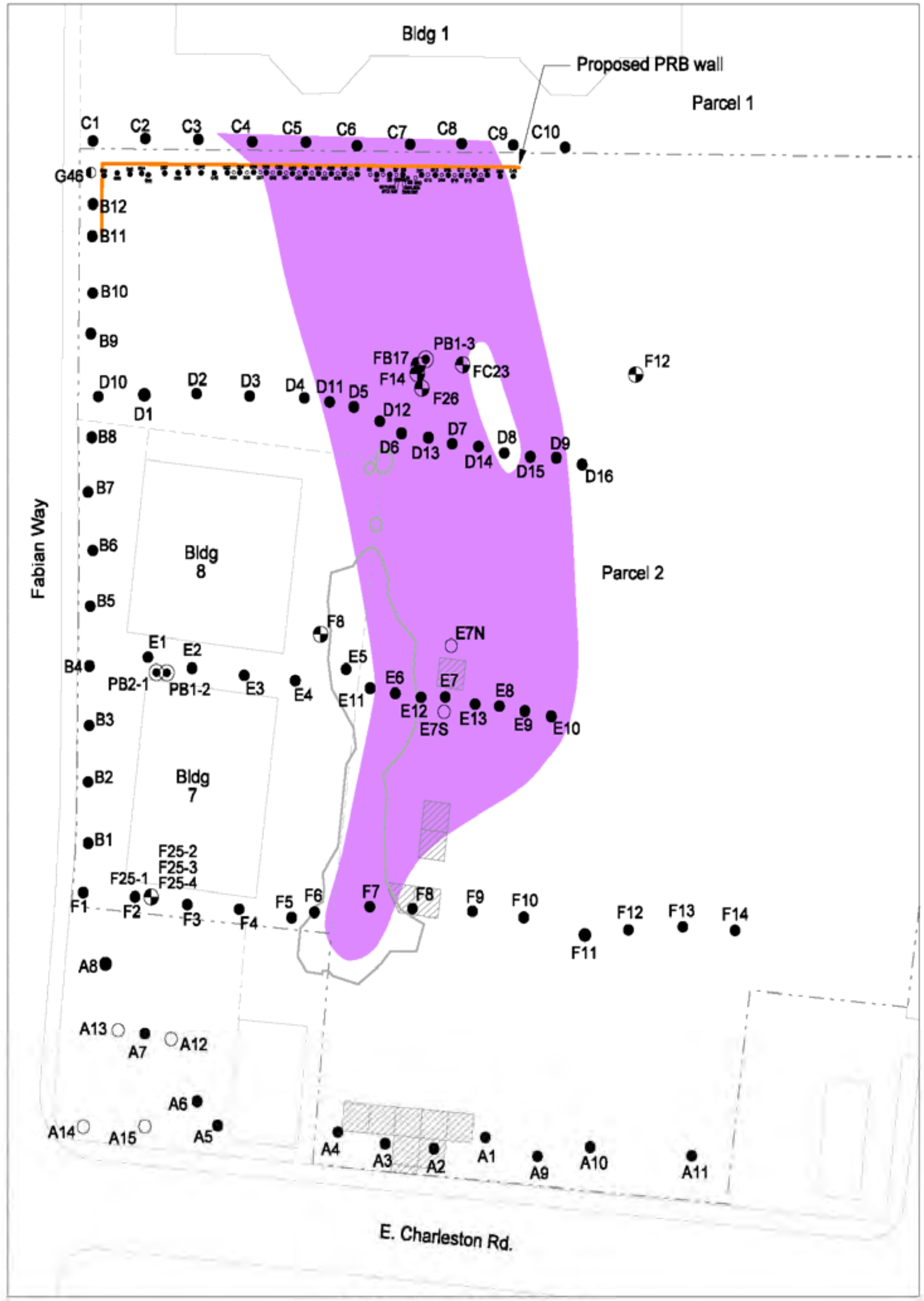
## 8 to 15 feet bgs




8-15 Feet Below Ground Surface

PCE > 100 ppb

15 to 40 feet bgs




15-40 Feet Below Ground Surface

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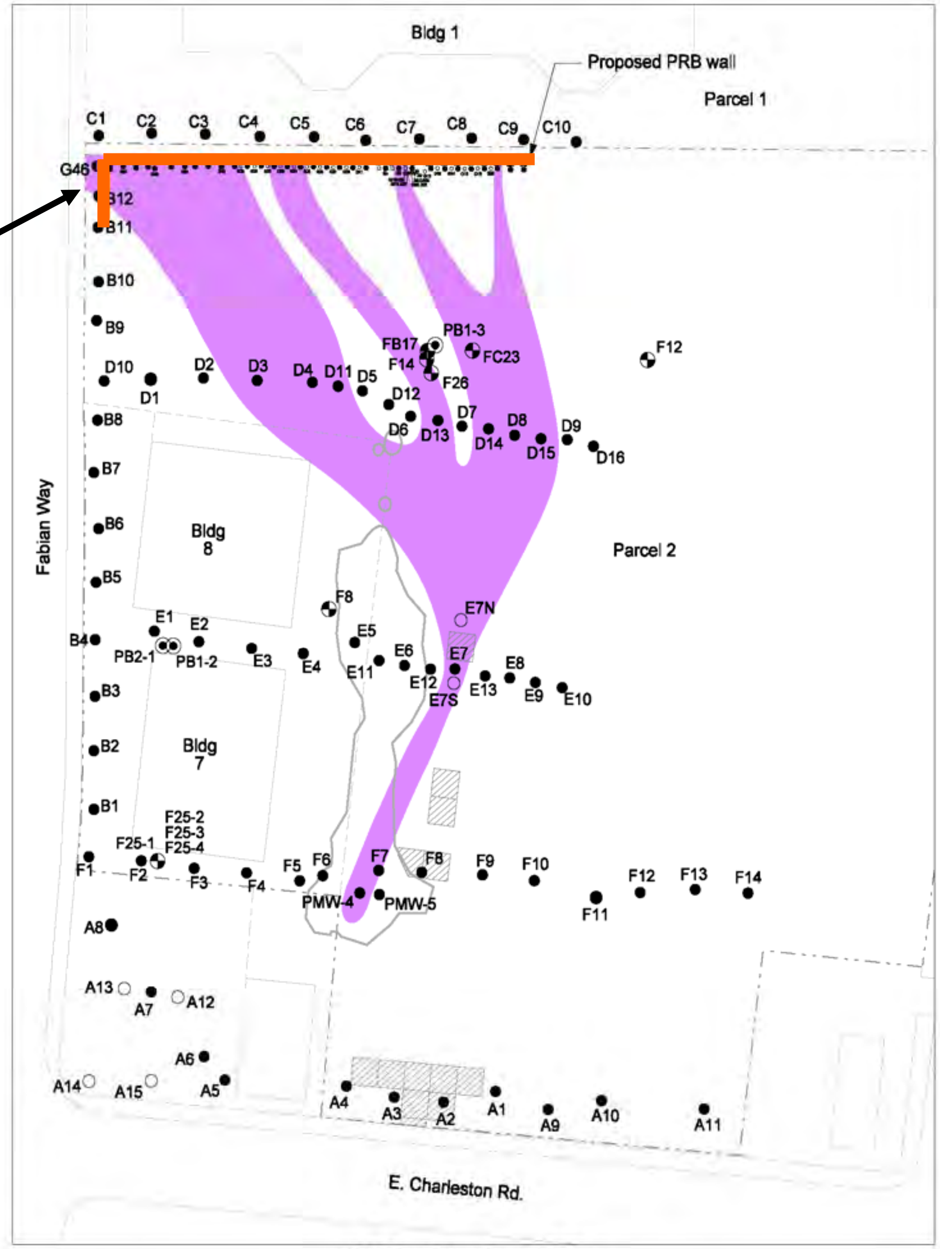
**PRB**

PCE > 100 ppb

40 to 55 feet bgs




40-55 Feet Below Ground Surface

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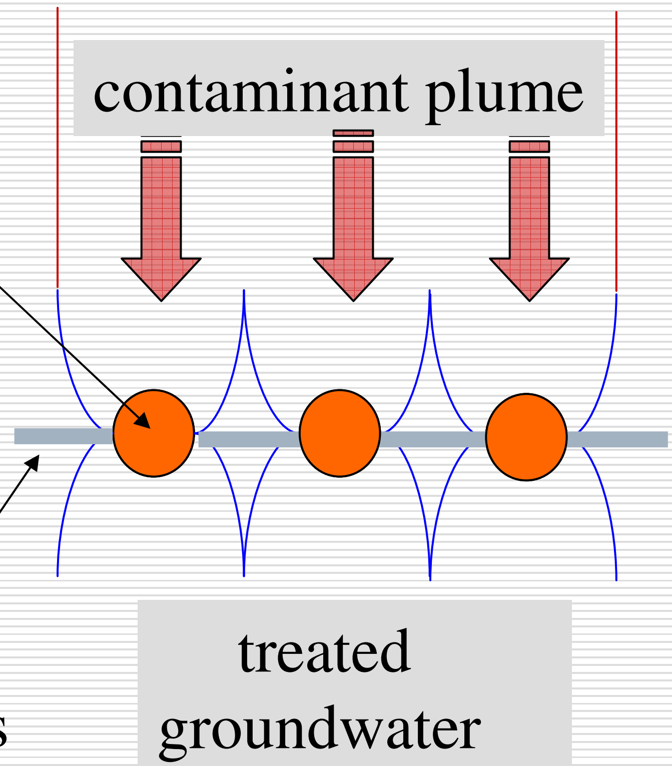
# Design Challenges

- 4 to 5 separate water-bearing zones
- Maintain hydraulic vertical separation of different water-bearing zones
- Treatment area up to 60 feet deep
- 370 feet in length

# Multiple Funnel-and-Gate Design Concept




**<u>ZVI gates</u>**
3 ft diameter multi-layered caissons

**<u>Slurry wall funnels</u>**
370 ft long continuous slurry wall

Caisson gates can be installed with multiple vertically-separated treatment zones Possible up to 100' deep.

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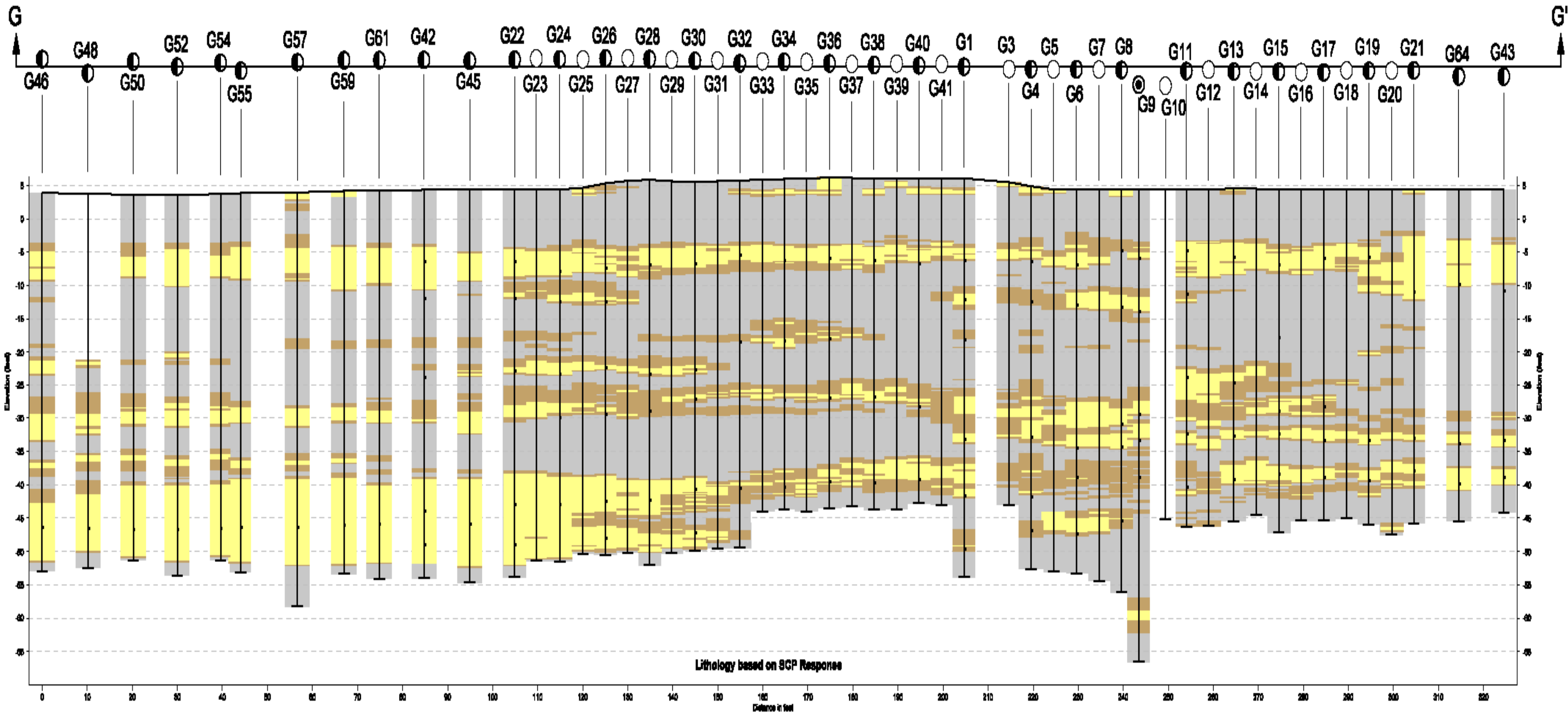
# Cross-section Along PRB

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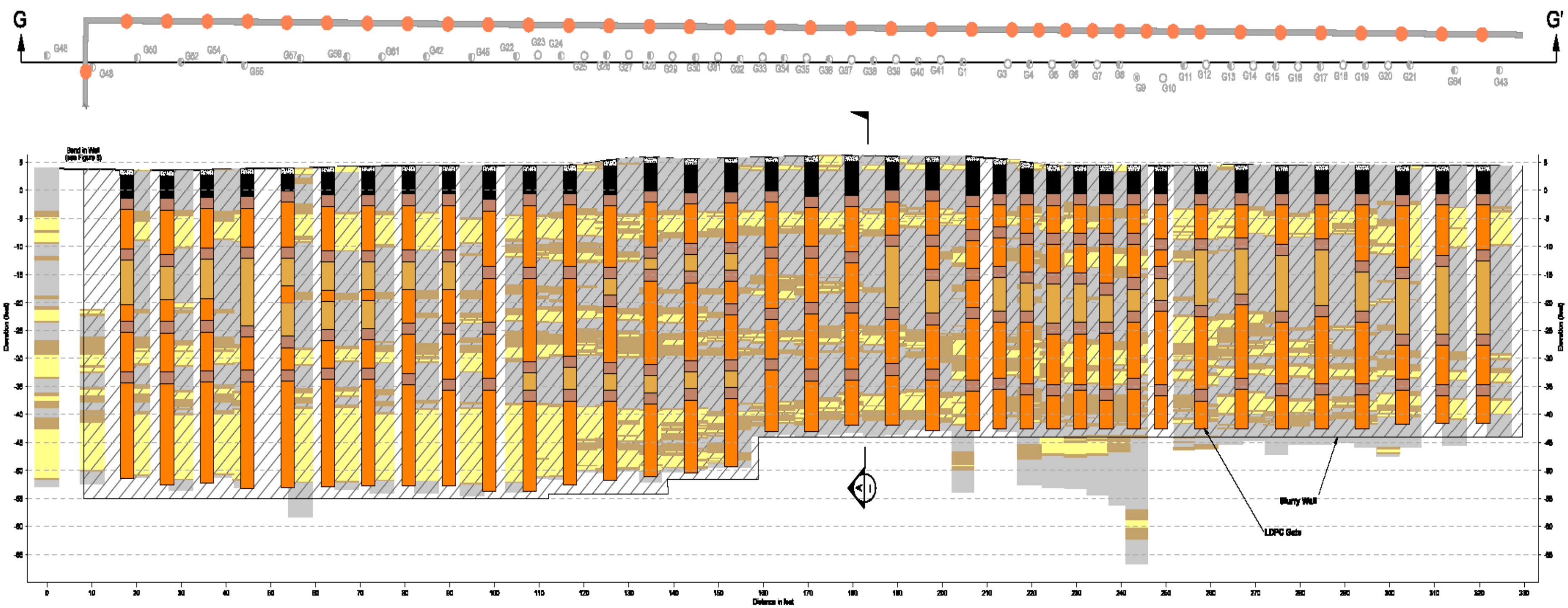
# PRB Design

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# PRB Design

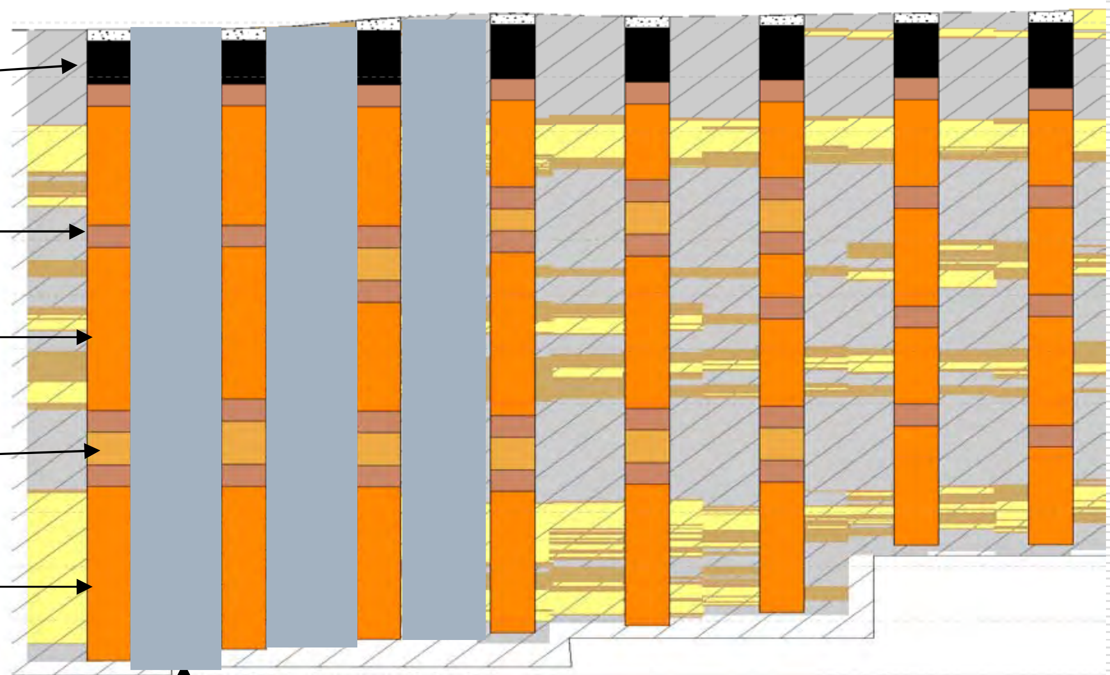
Cement seal

Bentonite seals

50% ZVI-sand

10% ZVI-sand

50% ZVI-sand



Slurry wall panels between borings

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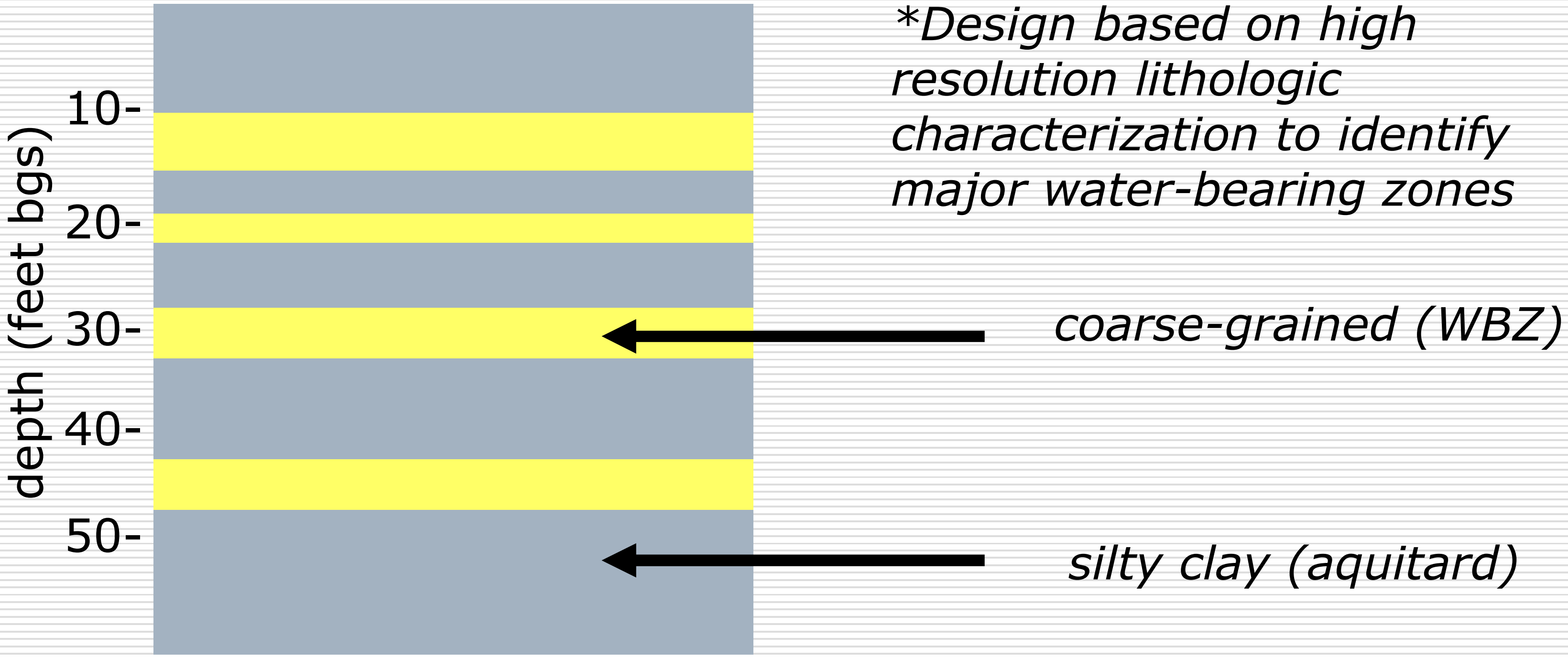
# Construction Methods – Step 1




**Design based on high resolution lithologic characterization to identify major water-bearing zones*

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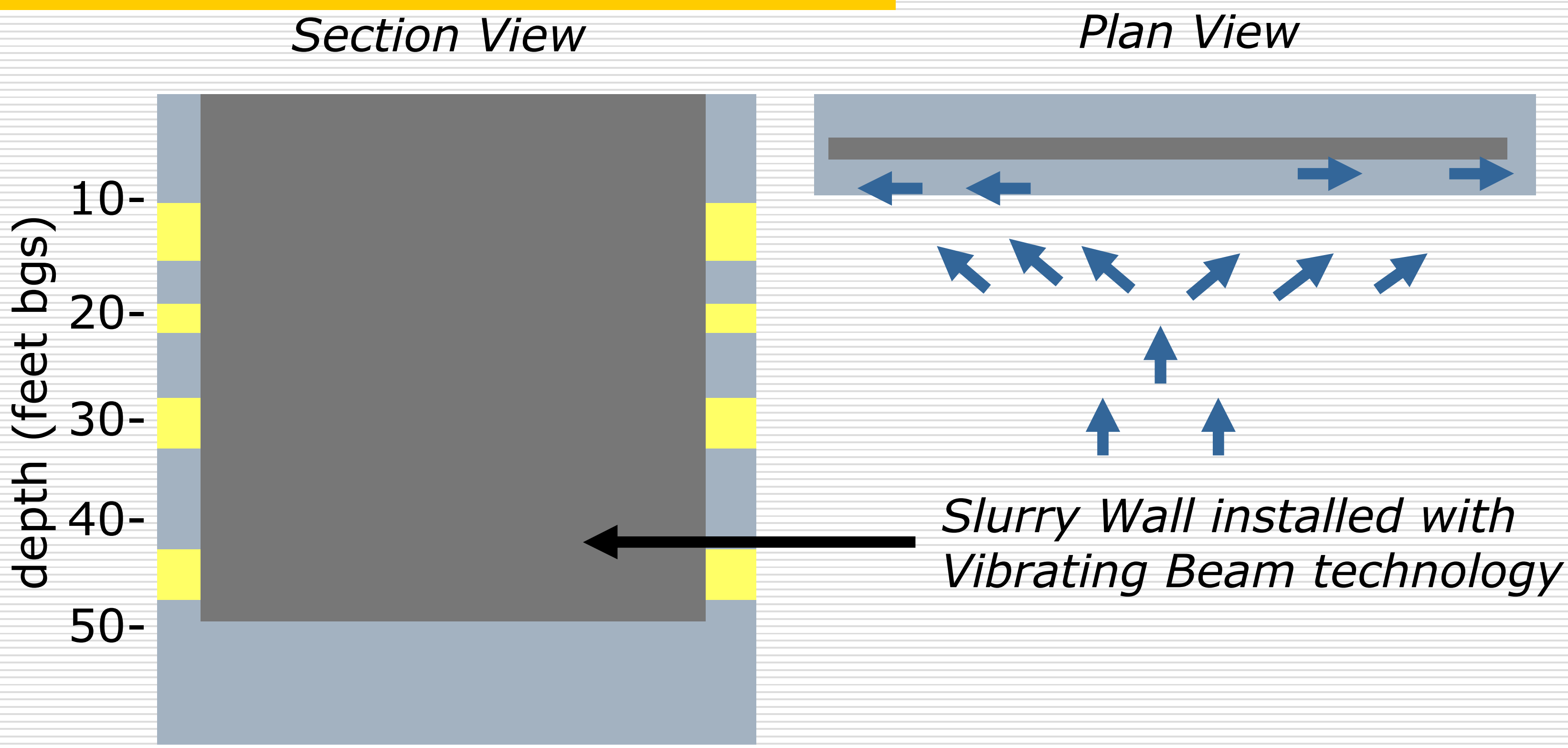
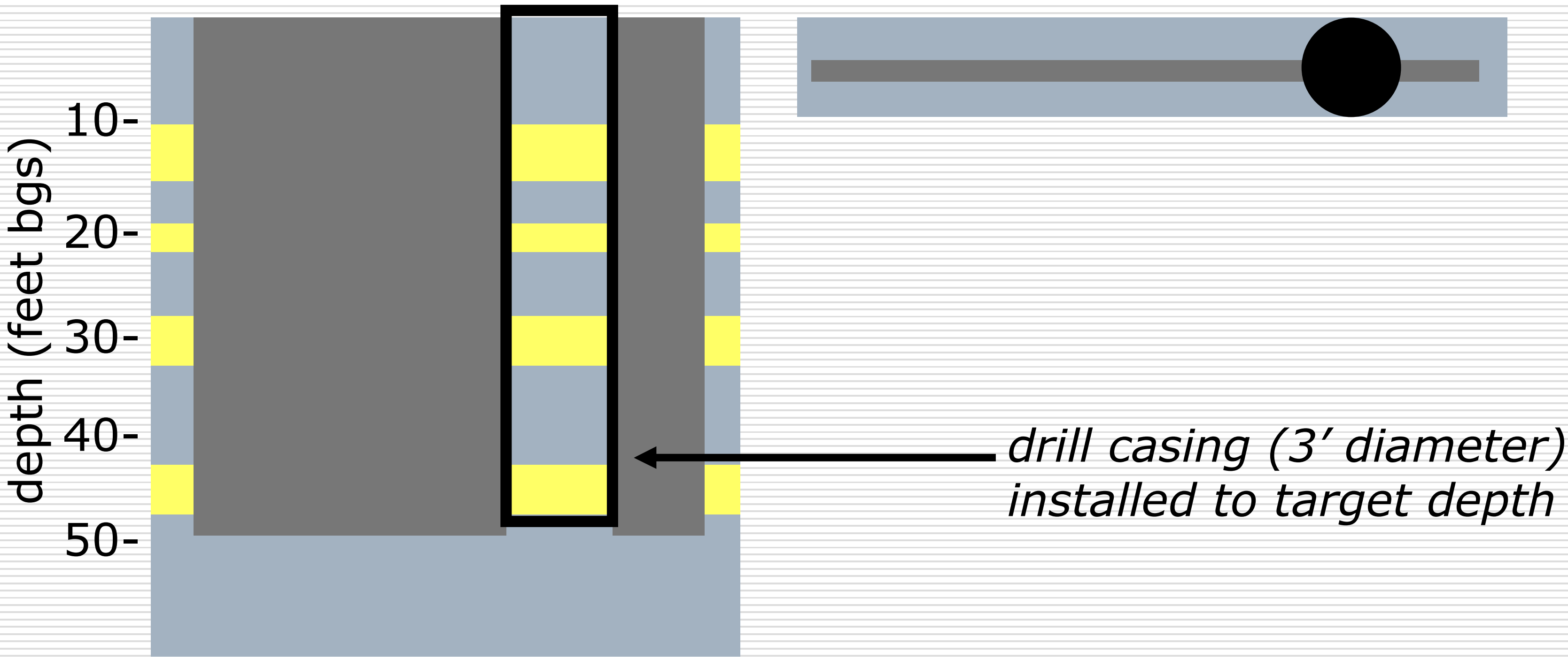
# Construction Methods – Step 2



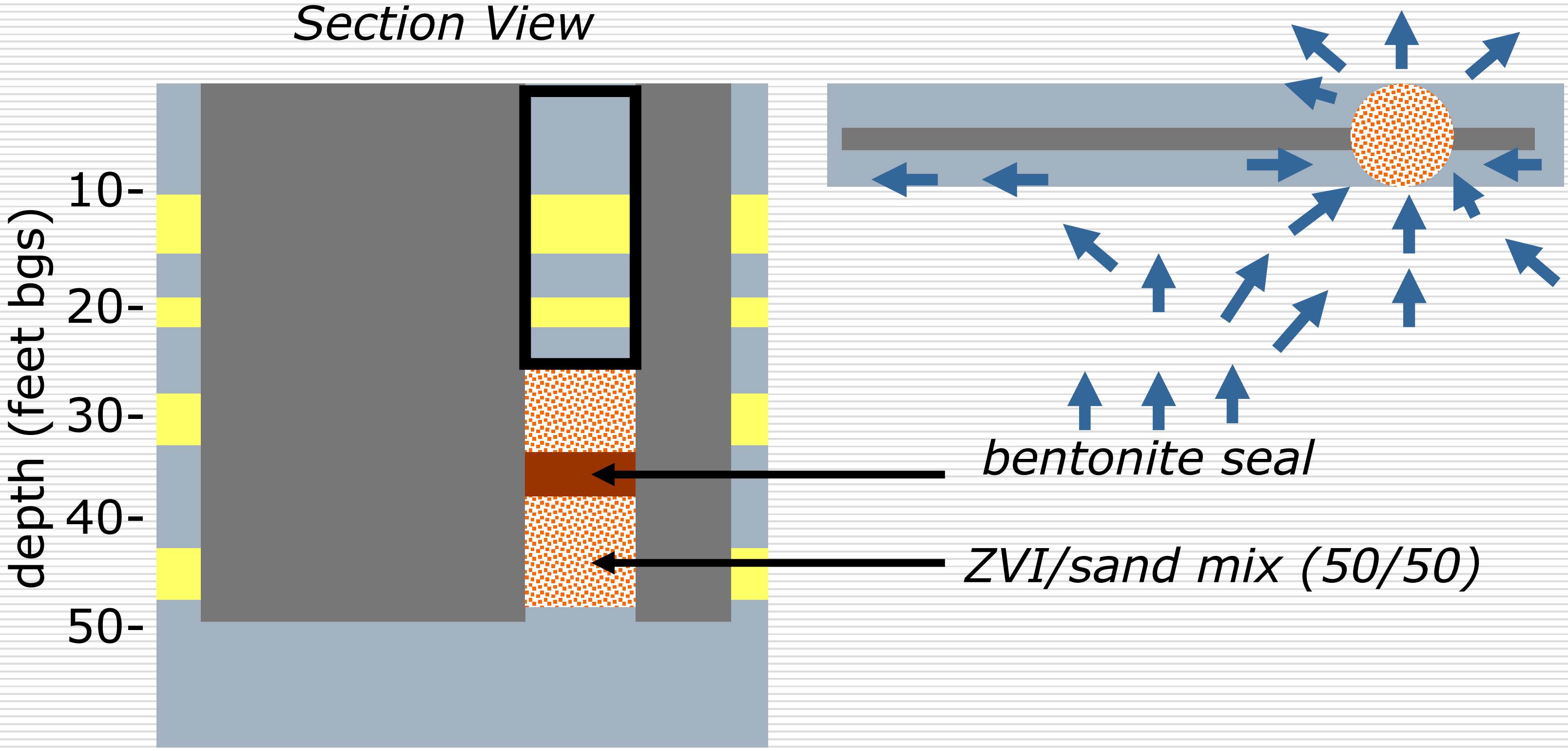

*A thin slurry wall is installed across the PRB alignment to divert gw flow*

# Construction Methods – Step 3



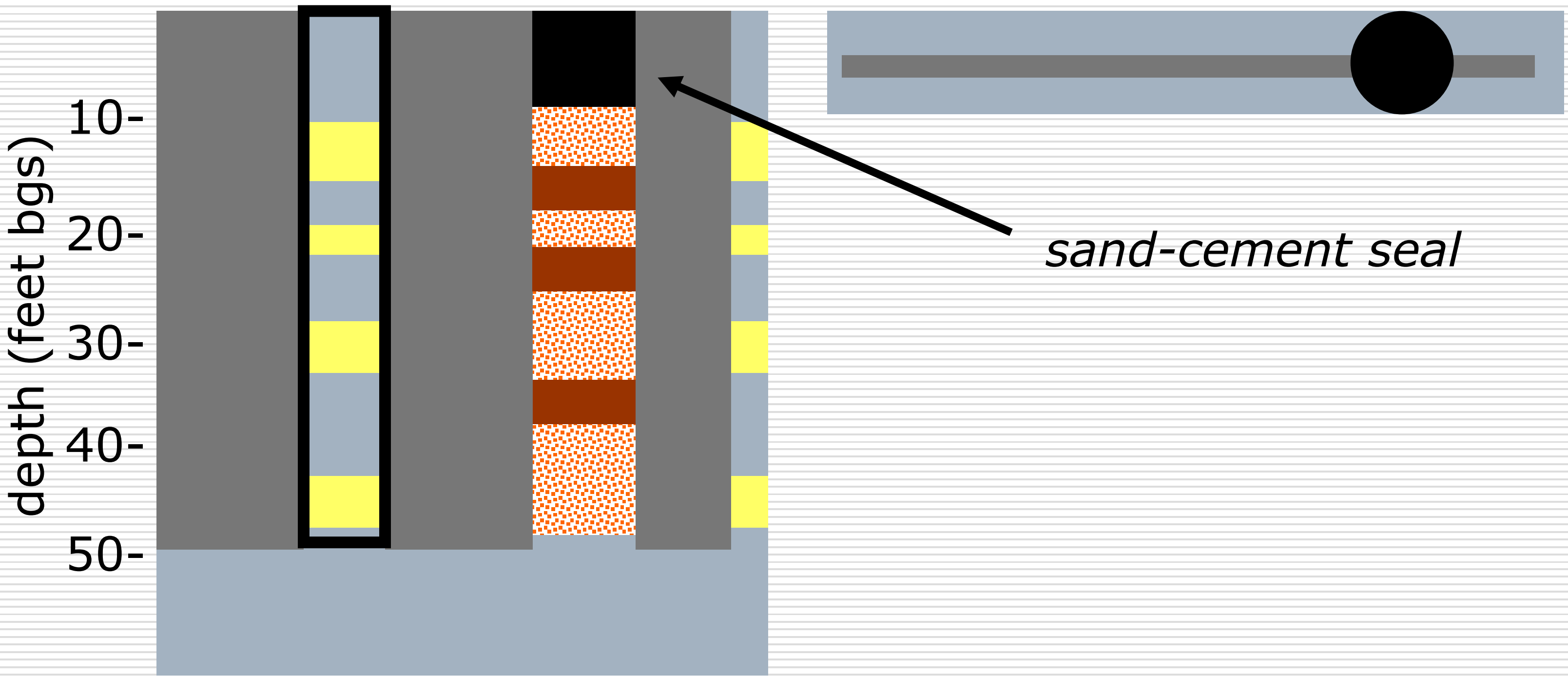

*A section of slurry wall is drilled out to allow for emplacement of ZVI and bentonite layers*

# Construction Methods – Step 4



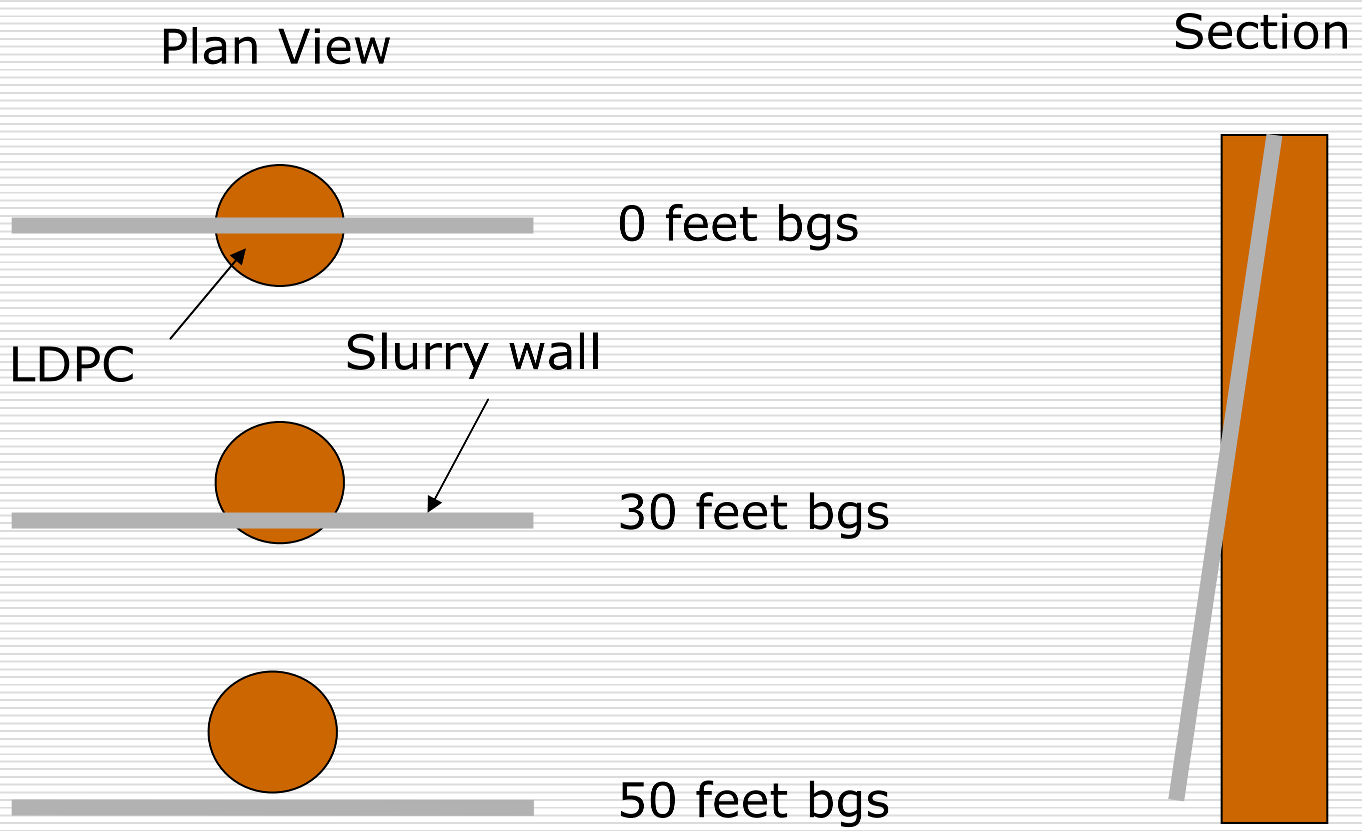

*Emplacement of ZVI and bentonite layers, flow through boring occurs*

# Construction Methods – Step 5




*Drilling of adjacent boring*

# Possible Deviation Issues



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COLM
BG40

# Construction Summary

| | |
|---|---|
| **GENERAL** | |
| Construction period | 56 days |
| **VIBRATING BEAM BARRIER WALL** | |
| Total length | 371 feet |
| Maximum depth | 60 feet |
| Minimum depth | 48.5 feet |
| Total square feet of wall | 20,480 square feet |
| Slurry produced | 13,699 cubic feet |
| Excess slurry disposed off-site | 6,460 cubic feet |
| Average thickness of slurry wall[3] | 5.8 inches |

# Construction Summary

| LARGE DIAMETER PERMEABLE COLUMNS | |
|---|---|
| Diameter of LDPCs | 36 inches |
| Number of LDPCs | 39 |
| Number of Treatment Gates | 172 |
| Total volume of ZVI/sand Used | 385 cubic yards |
| Total Volume of Bentonite Used | 100 cubic yards |

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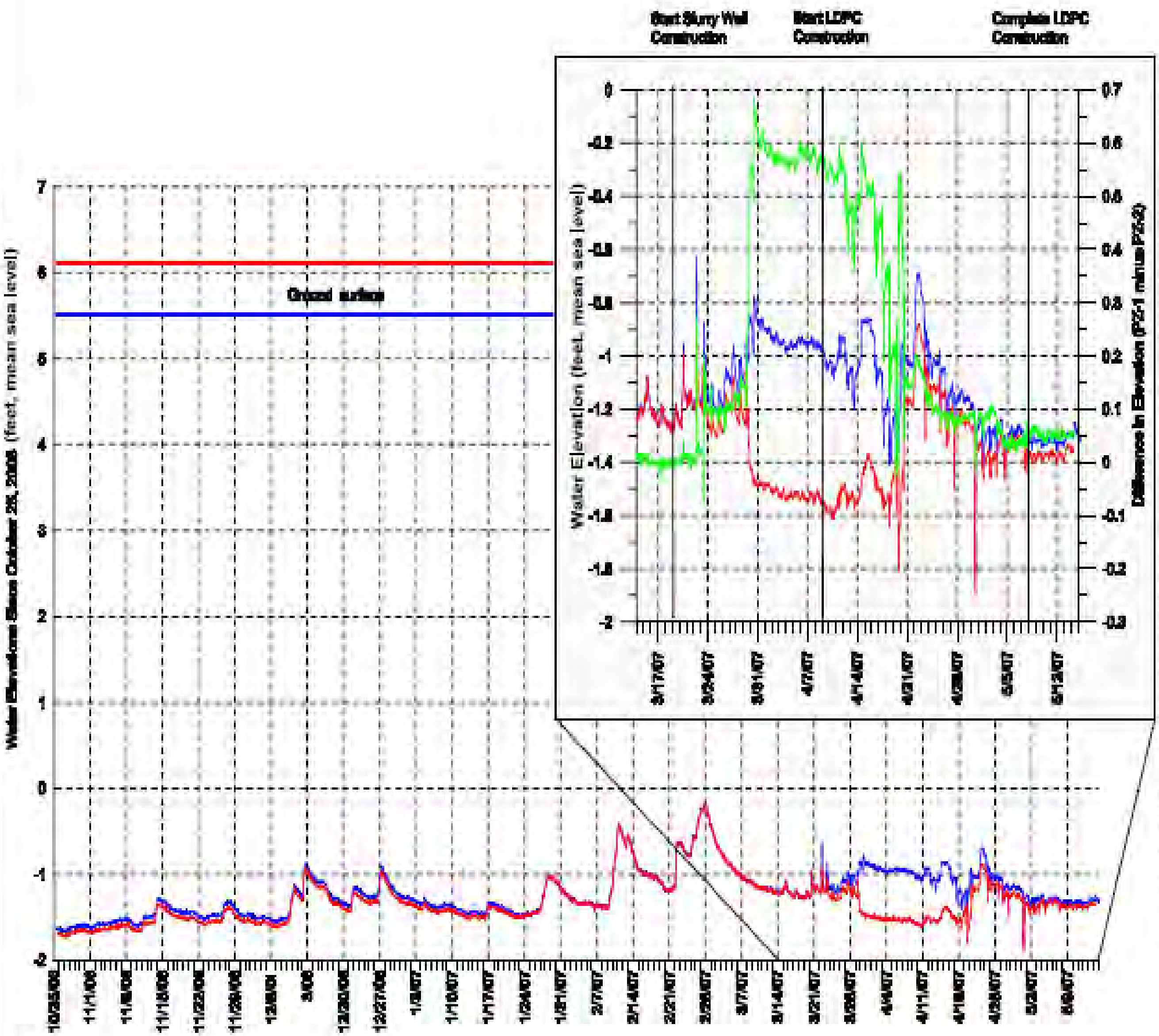
# Performance Summary

- Piezometers installed prior to construction upgradient and downgradient of PRB
- Water level response
  - After slurry wall
  - After LDPC installation
- Groundwater chemistry




Rain Events

| Date | Rain (inches) |
|---|---|
| 11/25/2006 | 0.01 |
| 11/26/2006 | 0.16 |
| 11/27/2006 | 0.07 |
| 12/8/2006 | 0.14 |
| 12/9/2006 | 0.40 |
| 12/10/2006 | 0.14 |
| 12/12/2006 | 0.58 |
| 12/15/2006 | 0.03 |
| 12/16/2006 | 0.01 |
| 12/21/2006 | 0.18 |
| 12/22/2006 | 0.01 |
| 12/26/2006 | 0.33 |
| 12/27/2006 | 0.16 |
| 12/31/2006 | 0.01 |
| 1/4/2007 | 0.11 |
| 1/16/2007 | 0.10 |
| 1/18/2007 | 0.01 |
| 1/26/2007 | 0.08 |
| 1/27/2007 | 0.30 |
| 1/28/2007 | 0.10 |
| 2/7/2007 | 0.03 |
| 2/8/2007 | 0.05 |
| 2/9/2007 | 0.20 |
| 2/10/2007 | 0.62 |
| 2/11/2007 | 0.08 |
| 2/12/2007 | 0.21 |
| 2/22/2007 | 0.55 |
| 2/23/2007 | 0.02 |
| 2/24/2007 | 0.15 |
| 2/25/2007 | 0.12 |
| 2/26/2007 | 0.47 |
| 2/27/2007 | 0.29 |
| 2/28/2007 | 0.03 |
| 3/20/2007 | 0.11 |
| 3/26/2007 | 0.09 |
| 4/11/2007 | 0.12 |
| 4/19/2007 | 0.30 |
| 4/20/2007 | 0.11 |
| 4/21/2007 | 0.06 |
| 4/22/2007 | 0.30 |
| 5/2/2007 | 0.02 |
| 5/3/2007 | 0.02 |
| 5/4/2007 | 0.02 |

Explanation

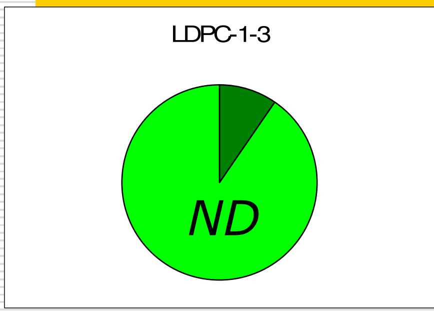
- PZ-1 water level (upgradient of the slurry wall)
- PZ-2 water level (downgradient of the slurry wall)
- Difference in water level elevations (inset only)

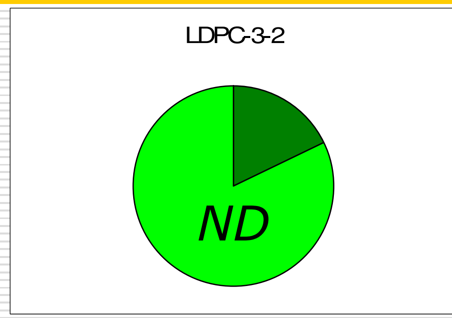
Note:
Groundwater elevation data for PZ-2 was adjusted to account for disturbance of the well casing during construction activities.

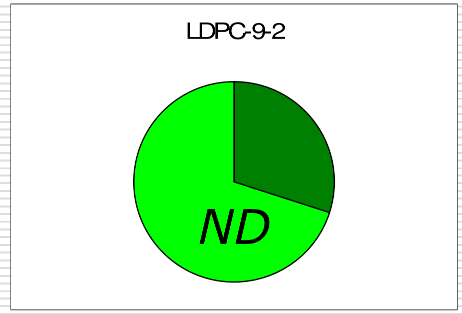
WATER LEVEL ELEVATIONS
PZ-1 AND PZ-2
901 San Antonio Road, Parcel 2
Palo Alto, California

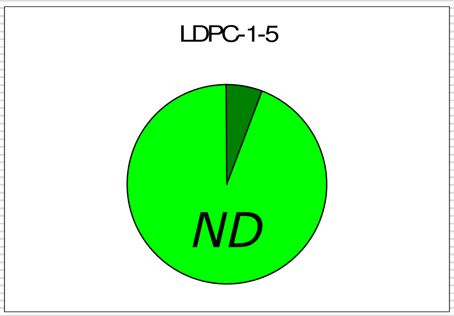
| By: MC | Date: 06/20/07 | Project No. 9311.005 |
|---|---|---|
| Geomatrix | | Figure H-1 |

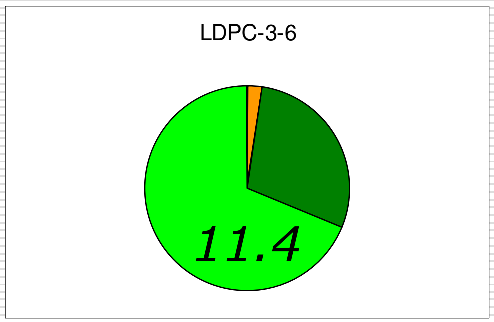
# First Round Monitoring Results (numerical values are total CVOCs)

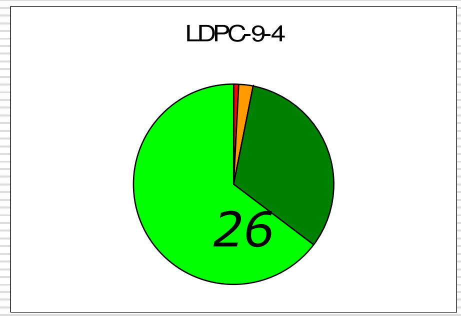


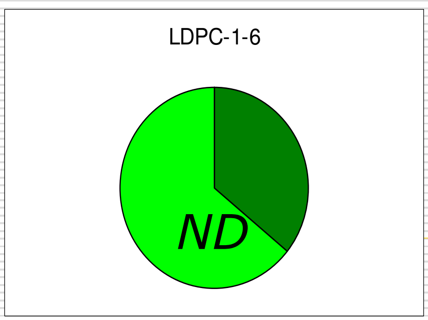



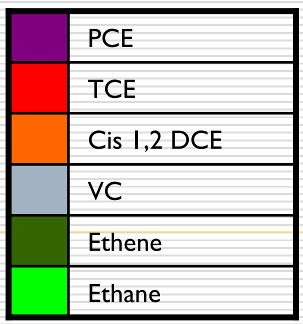



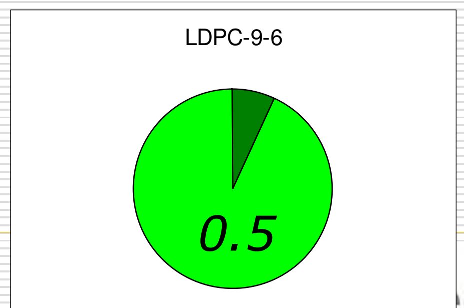



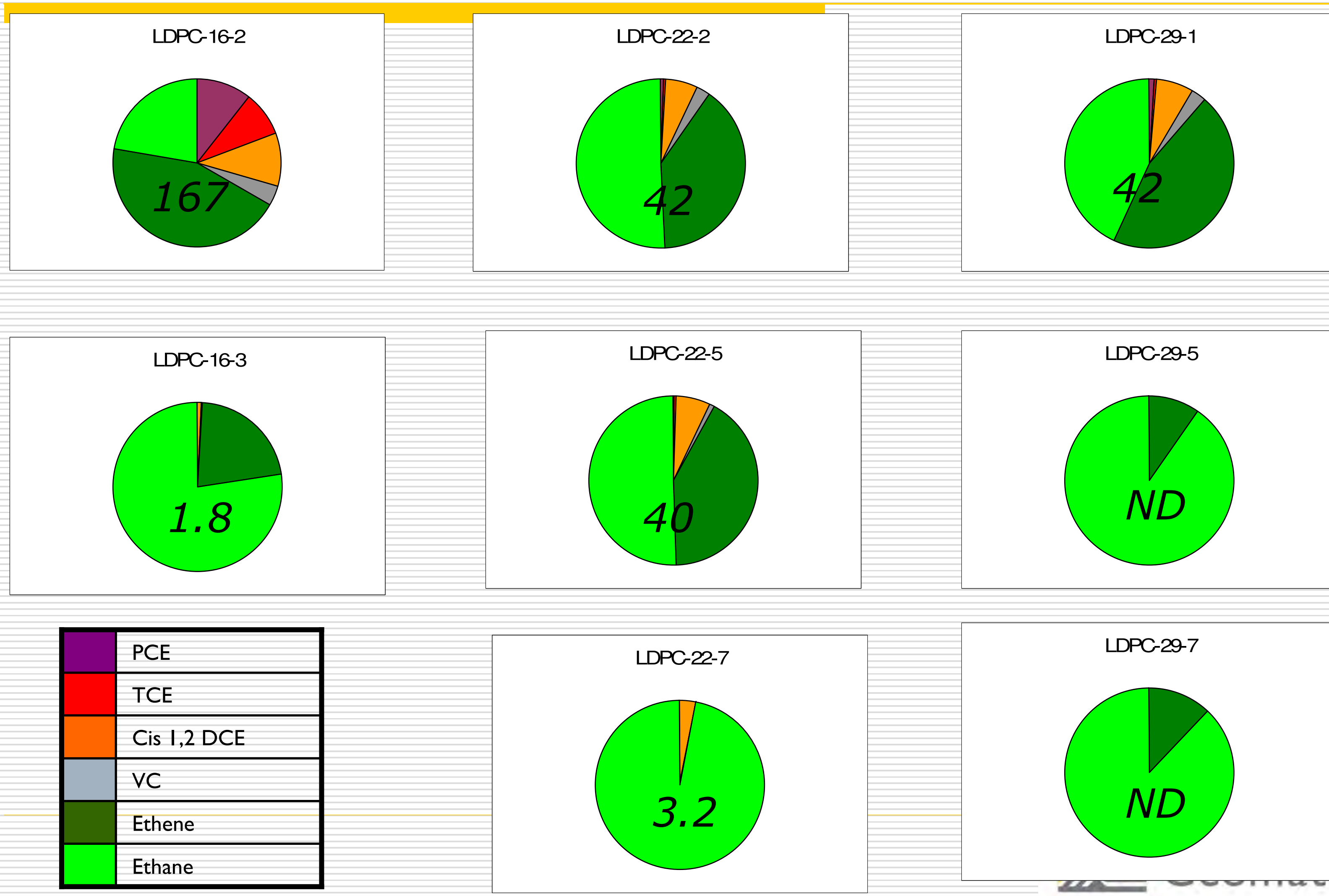



# First Round Monitoring Results



# Summary of VOC Removal

- Chlorinated VOCs low to non-detect in samples within PRB
- Calculated % Destruction is 99 to 100% in all but two sampling locations (80% and 89%)
- Data needs: Install upgradient and downgradient monitoring points

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- OTHER GMX TEAM MEMBERS

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