Local Applications of Innovative Groundwater Cleanup Using Zero Valent Metals

January 31, 2008

US EPA Region 9

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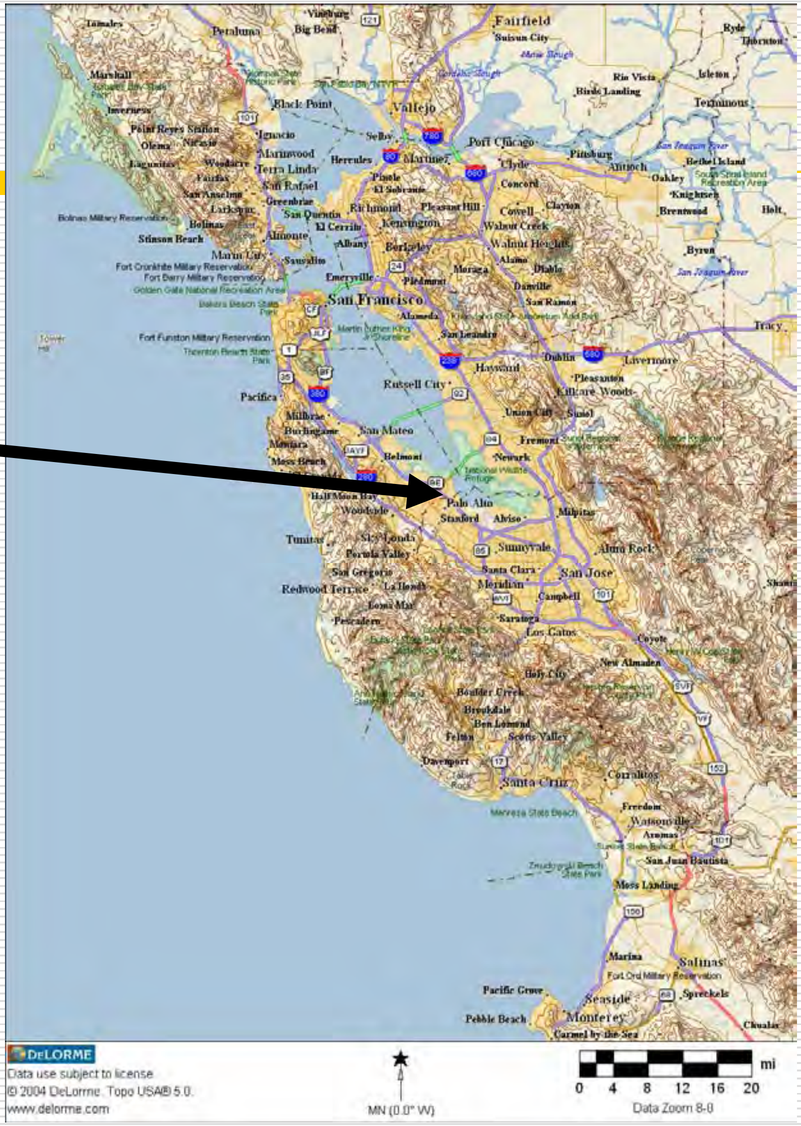
OUTLINE

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?

Site History – 20th Century

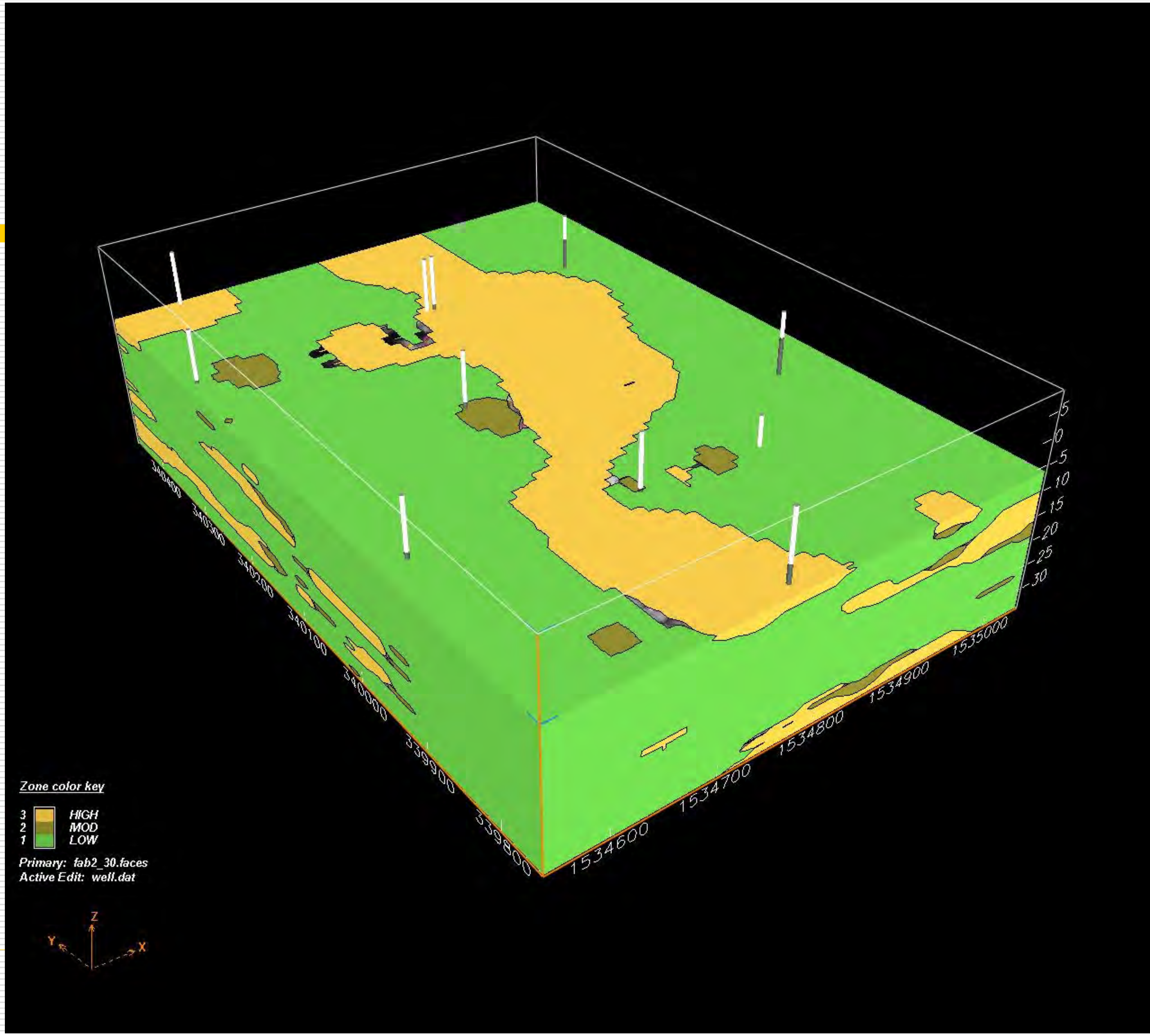
- Aerospace facility operated since the late 1950's
- Surface releases of PCE reportedly occurred along a fence line (weed control?)
- Characterization and GW Monitoring begins in the late 1980's (offsite plumes suspected)
- Soil remediation of source area in the mid-1990's (excavation of >5,000 cy with 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

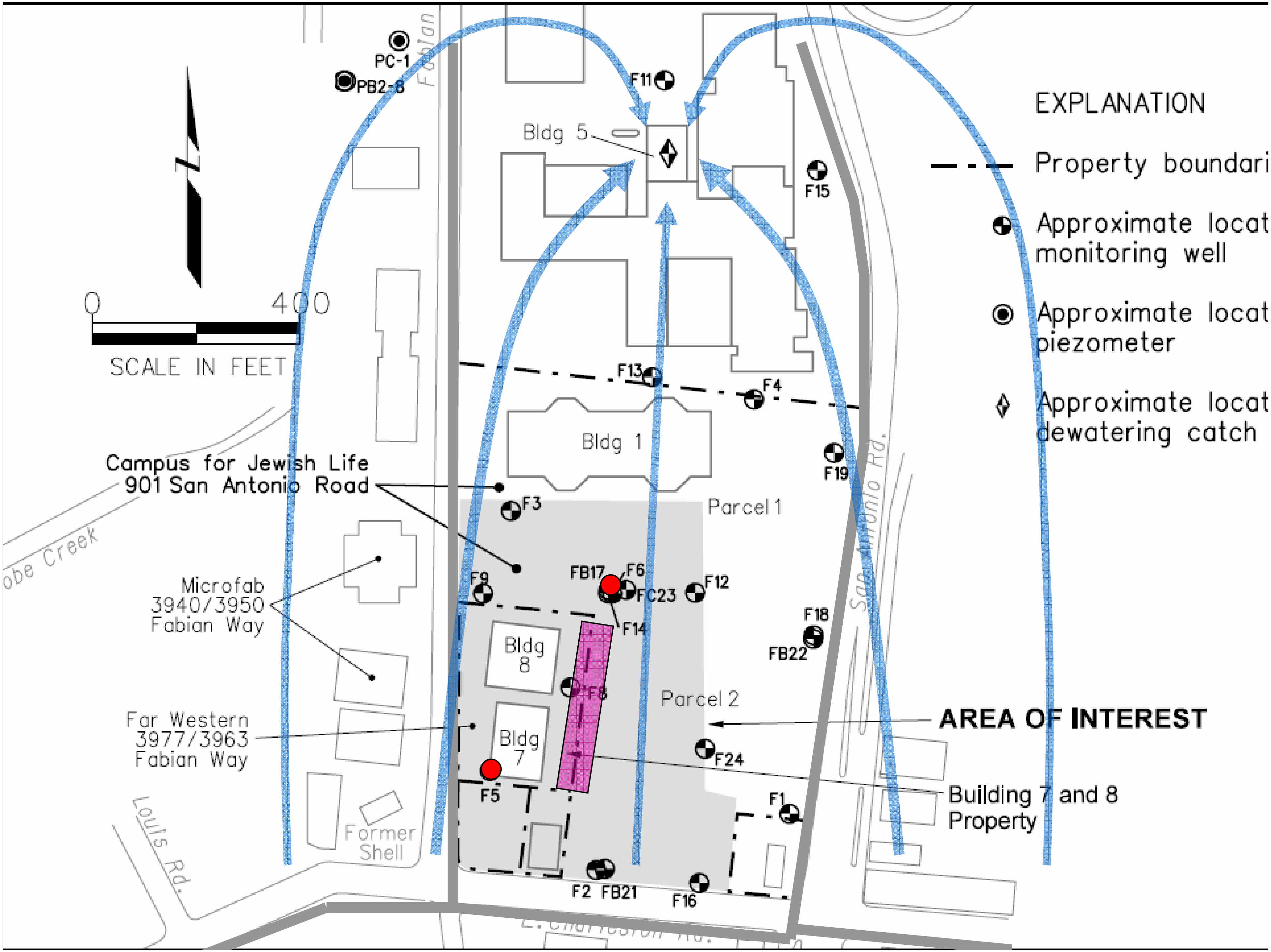


Zone color key
3 HIGH
2 MOD
1 LOW
Primary: fab2_30.faces
Active Edit: well.dat
340400
340300
340200
340100
340000
339900
339800
1534600
1534700
1534800
1534900
1535000
Z
Y
X

ix

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

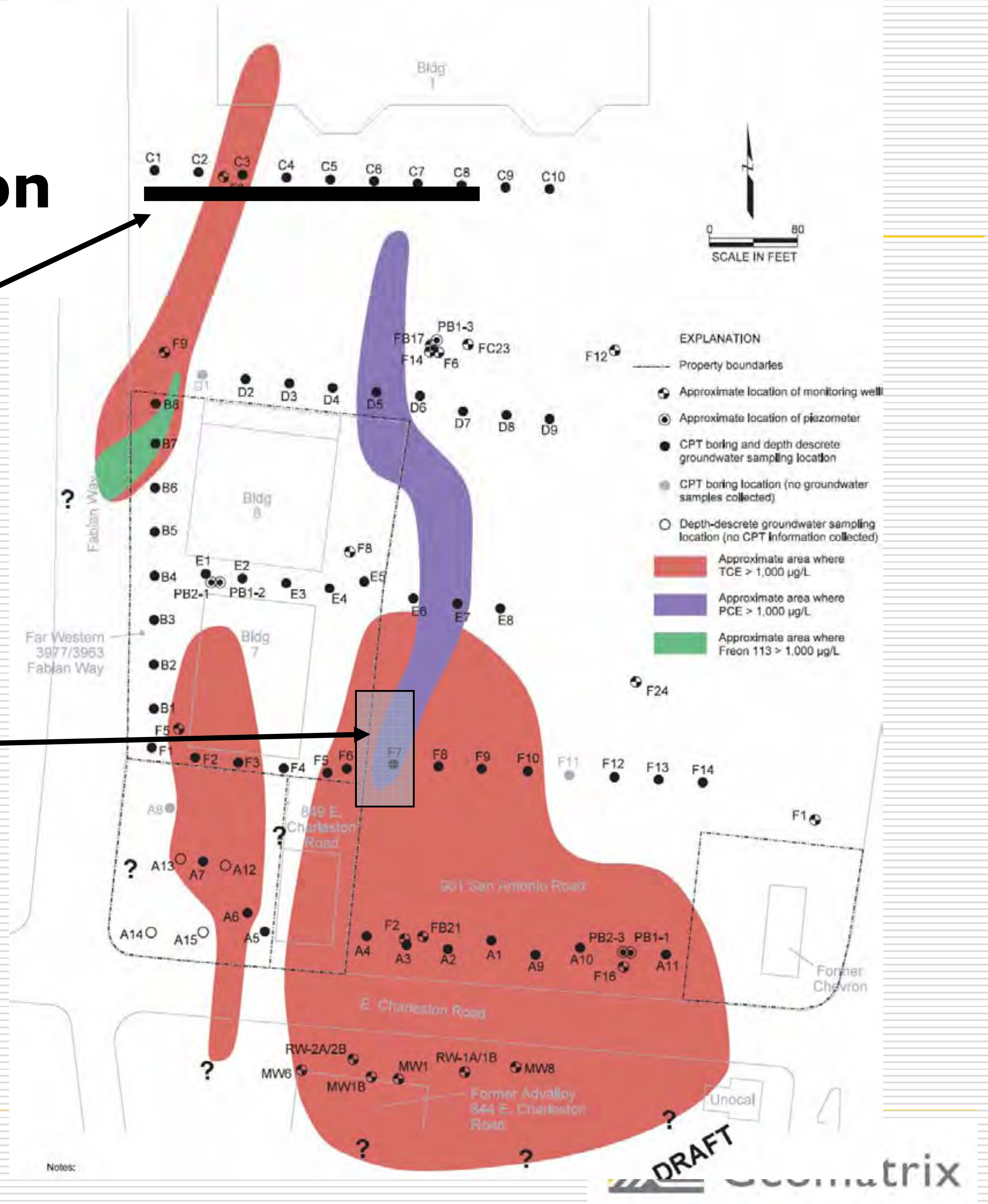


PC-1
PB2-8
Fabian
F11
Bldg 5
EXPLANATION
Property boundari
Approximate locat monitoring well
Approximate locat piezometer
Approximate locat dewatering catch
F15
0
400
SCALE IN FEET
F13
F4
Bldg 1
F19
Campus for Jewish Life
901 San Antonio Road
F3
Parcel 1
San Antonio Rd.
obe Creek
Microfab
3940/3950
Fabian Way
FB17
F6
F9
FC23
F12
F14
F18
FB22
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.

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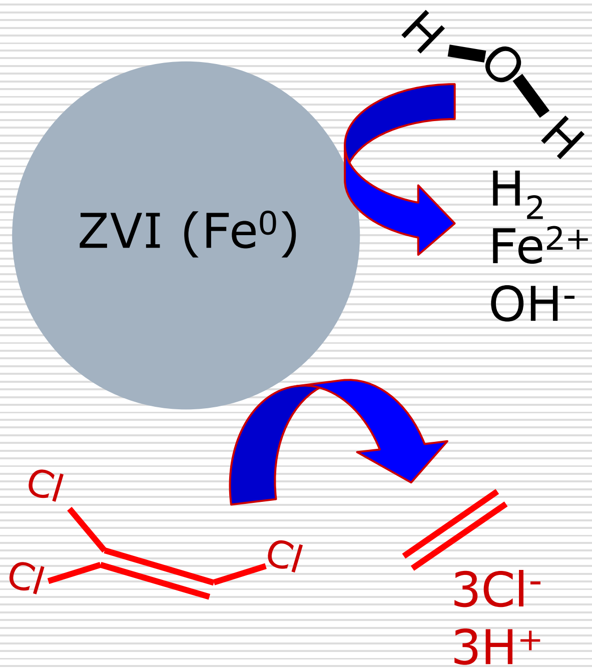
VOC Destruction on ZVI



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*

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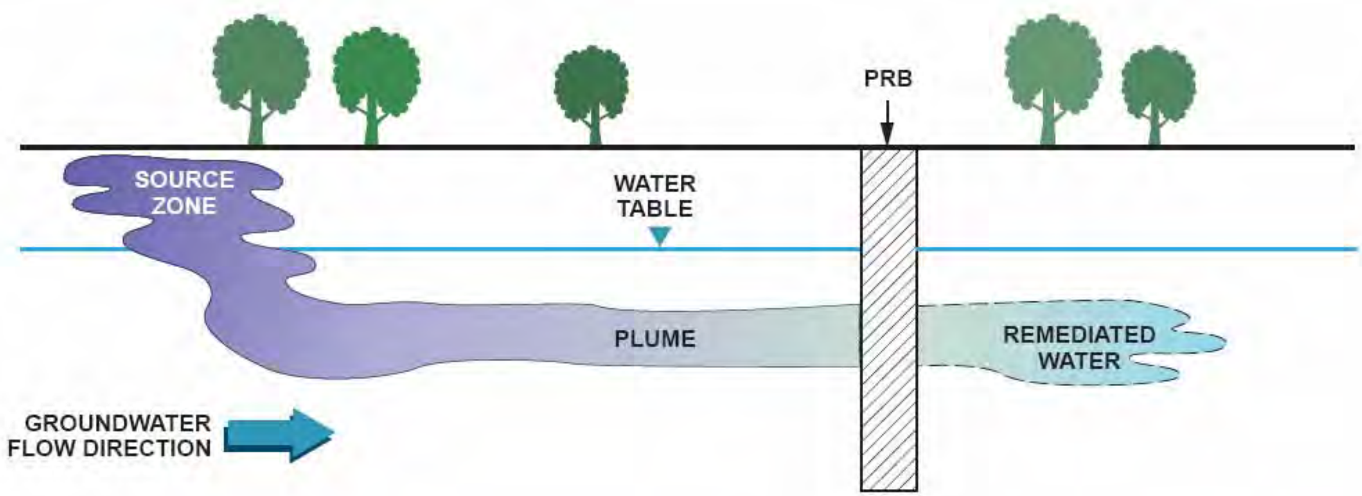
PRB composed of ZVI:

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

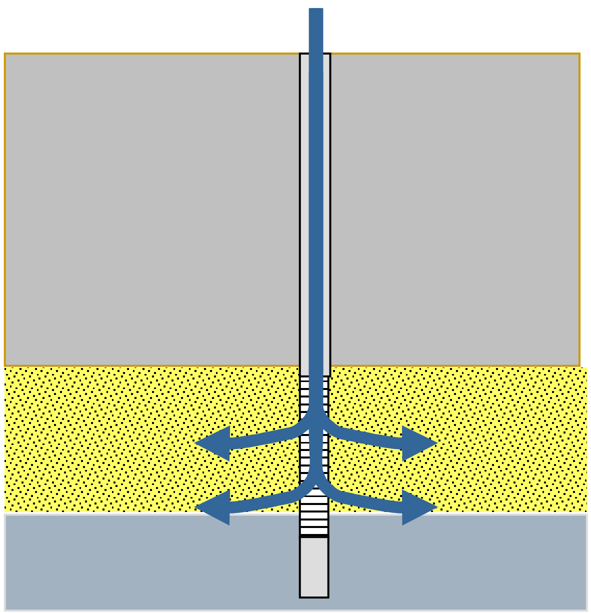


Metallic Nanoparticles for Groundwater Cleanup

- 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



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…

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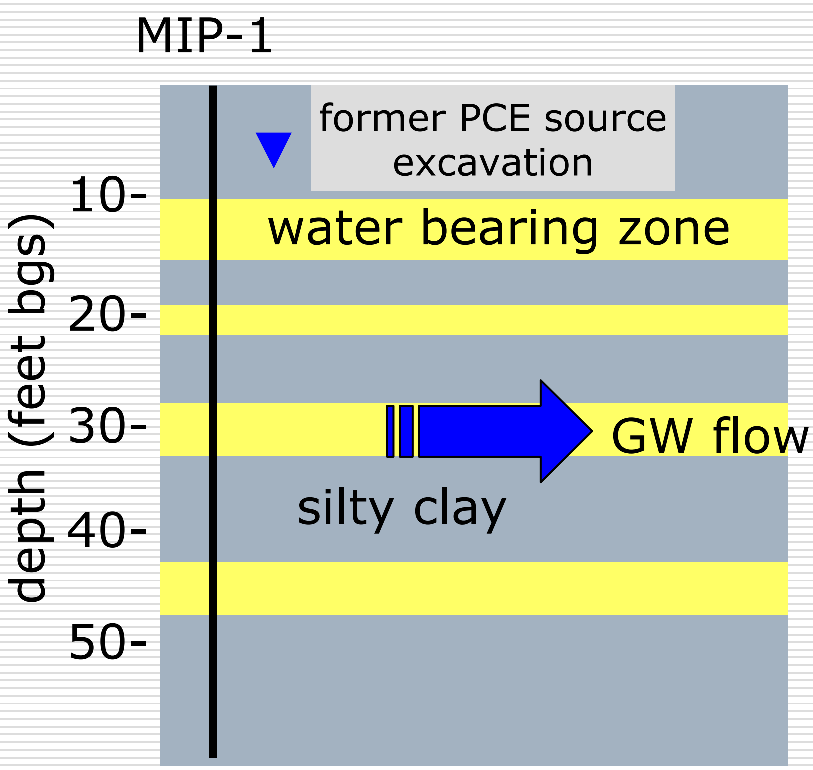
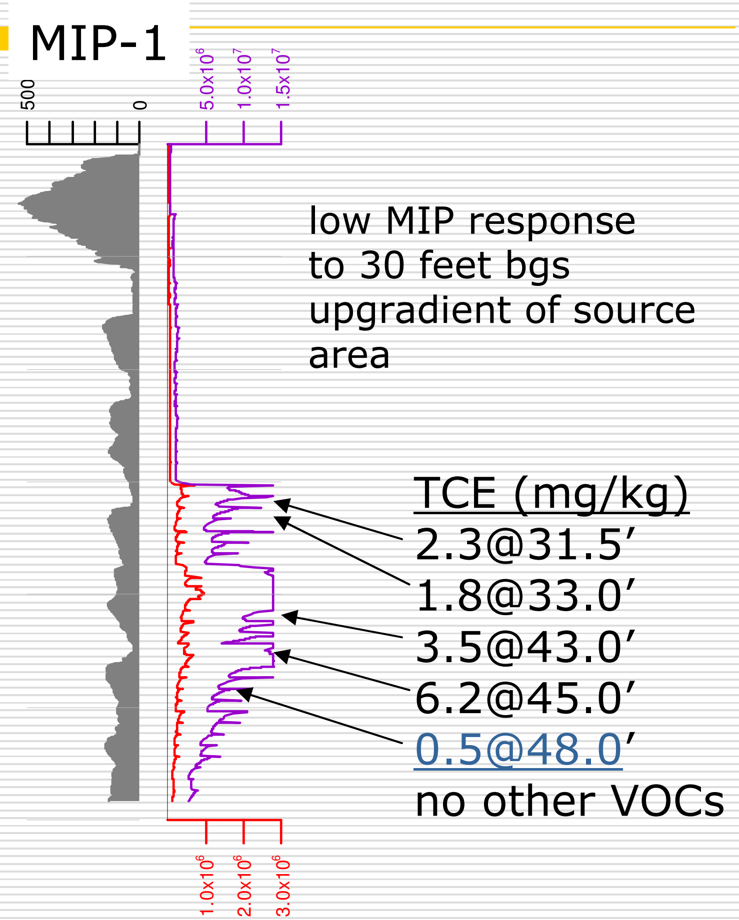
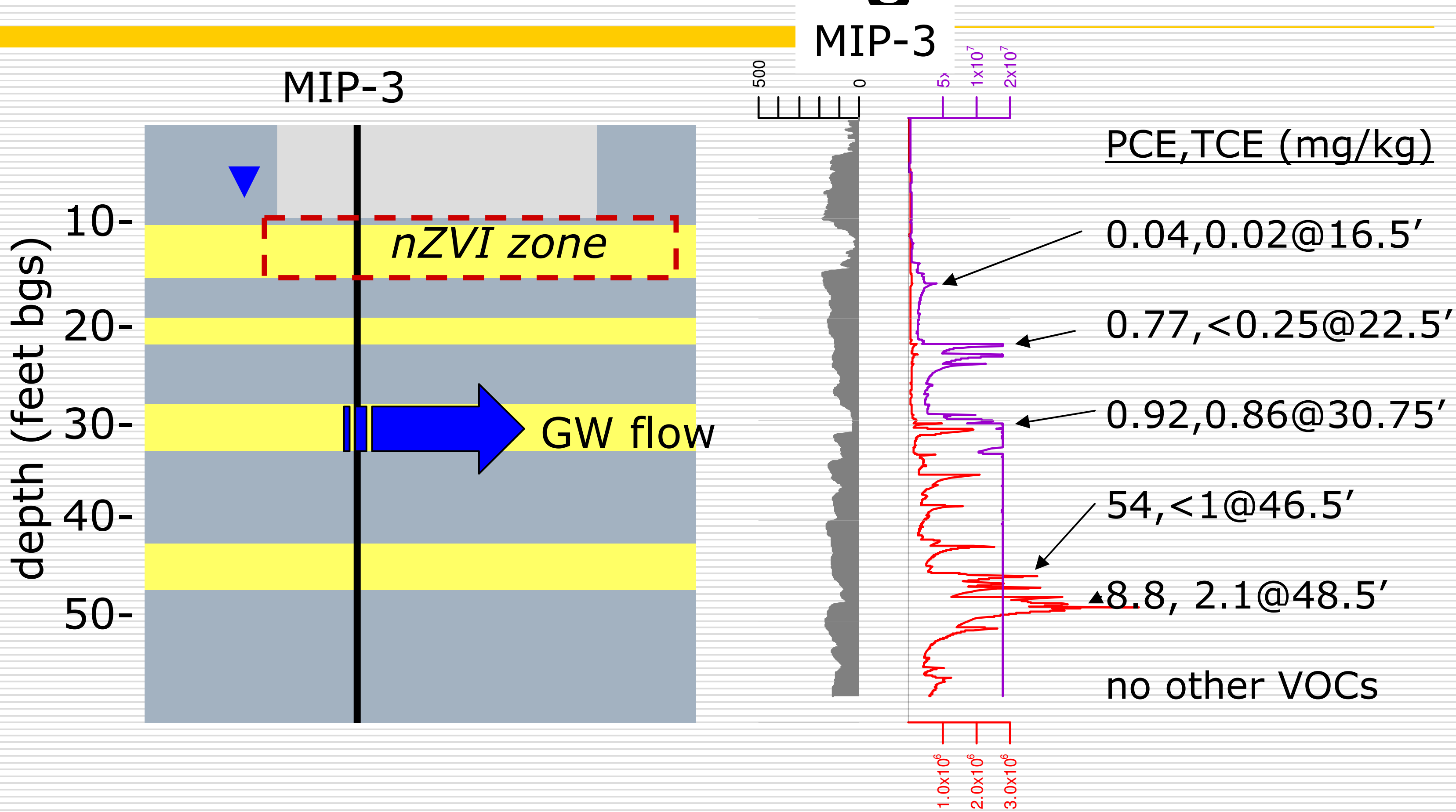
Source Area: Upgradient Plume





This MIP profile indicated the location of an offsite TCE plume

Source Area: Commingled Release



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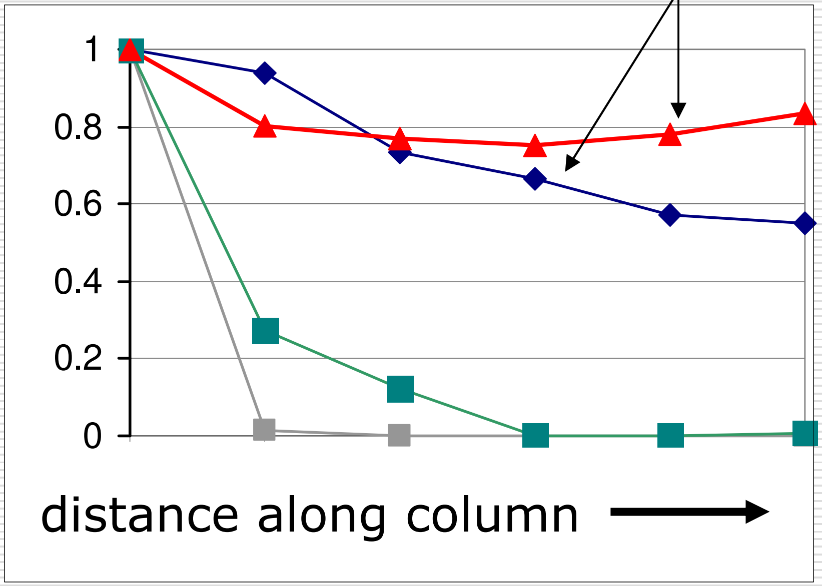
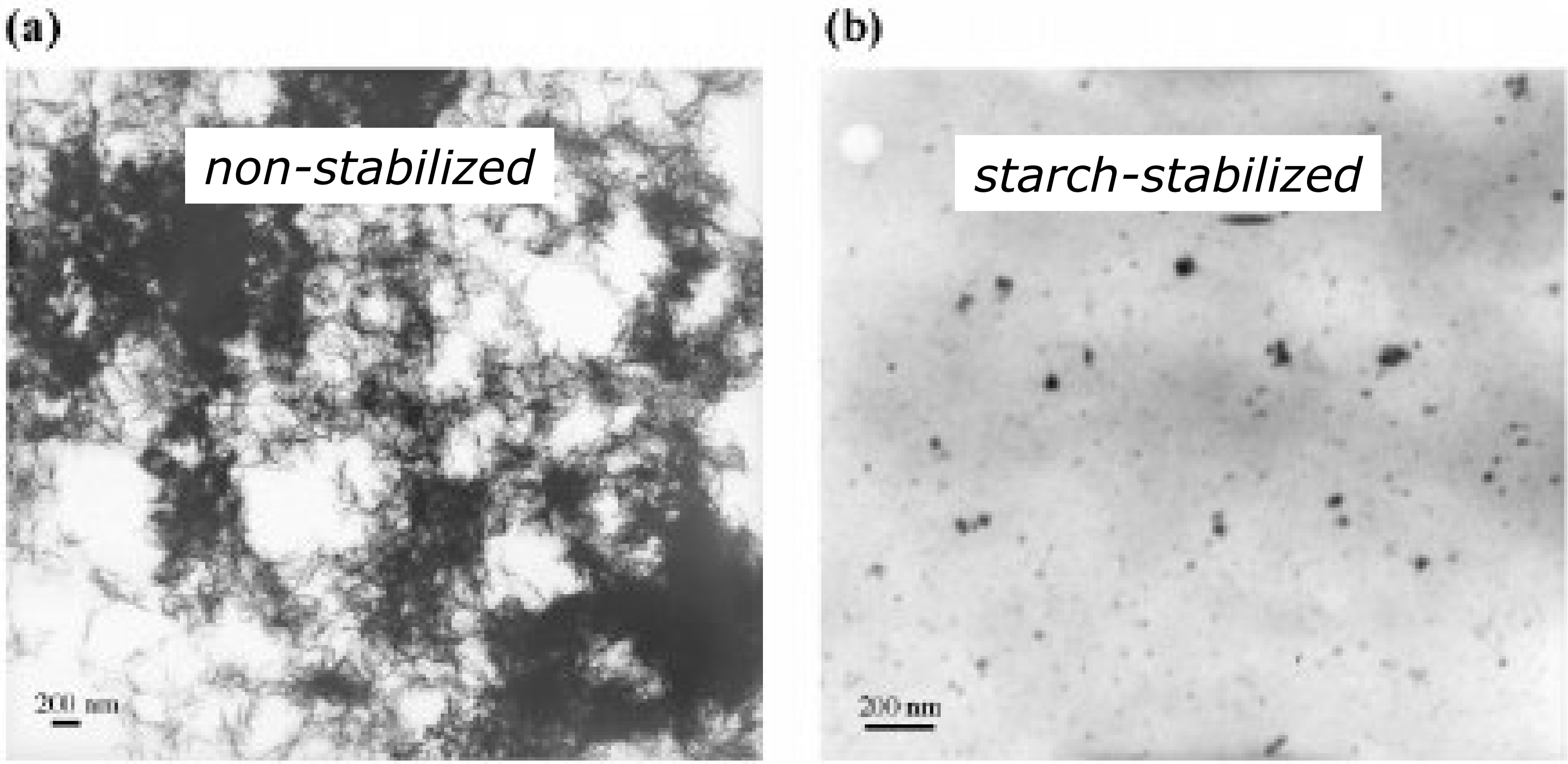
Nano-Scale Iron Column Tests

“starch-stabilized” nano iron



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

Synthesis of nZVI:

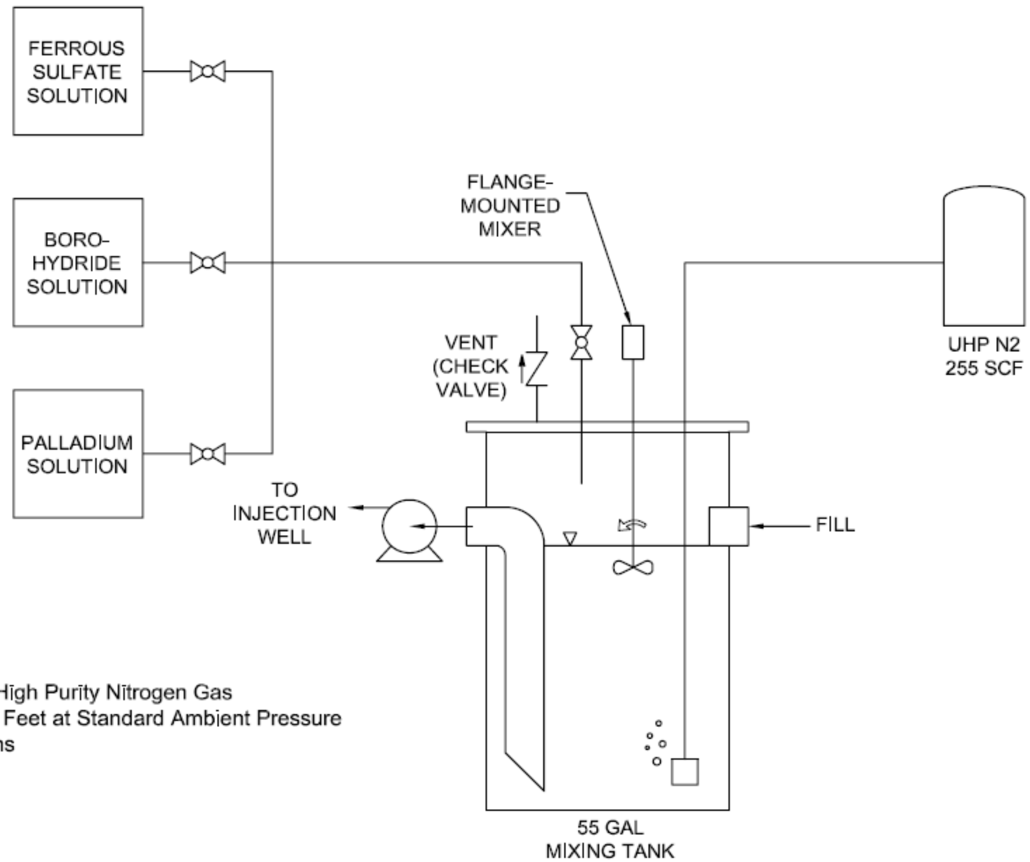
1. Prepare Starch (CMC 90K) and Ferrous Iron solution (remove O_2)
2. Reduce Ferrous Iron with Borohydride

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

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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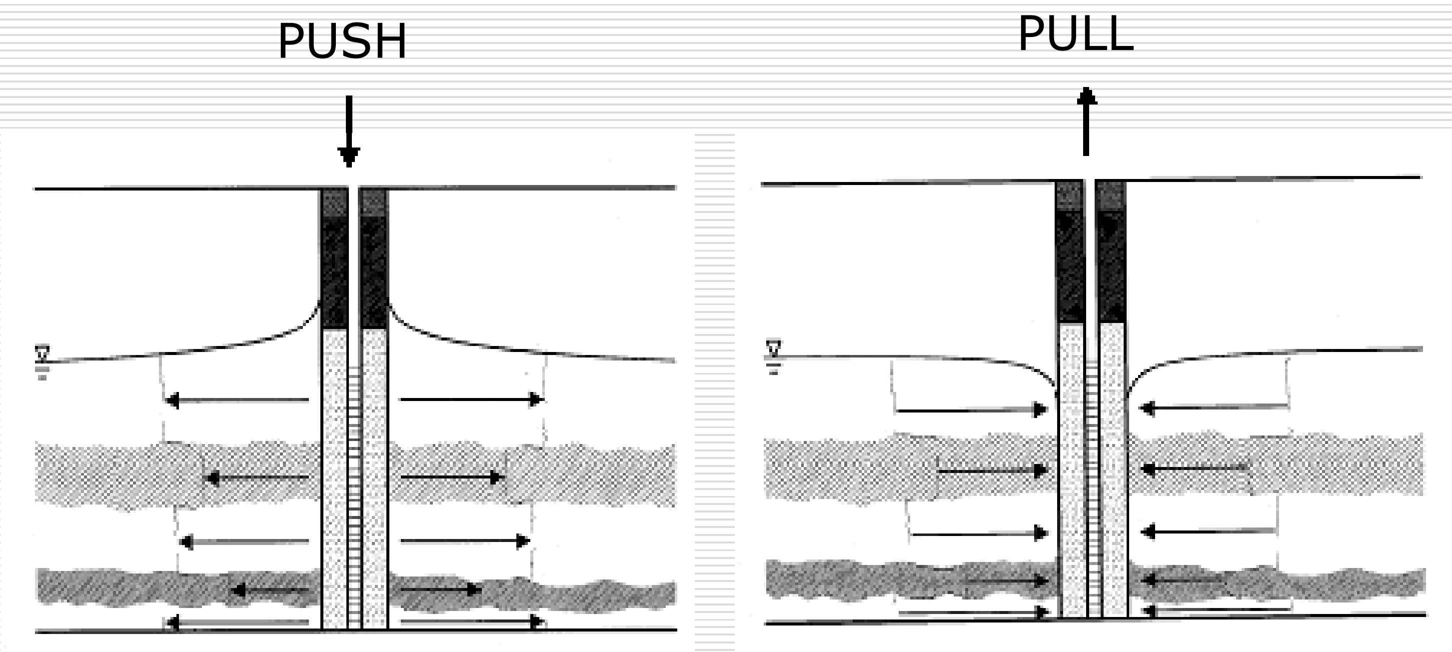
Summary of nZVI batches

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



FIGURES FROM OREGON STATE UNIVERSITY WEBSITE.

Injection Wellhead

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Push-Pull Tests

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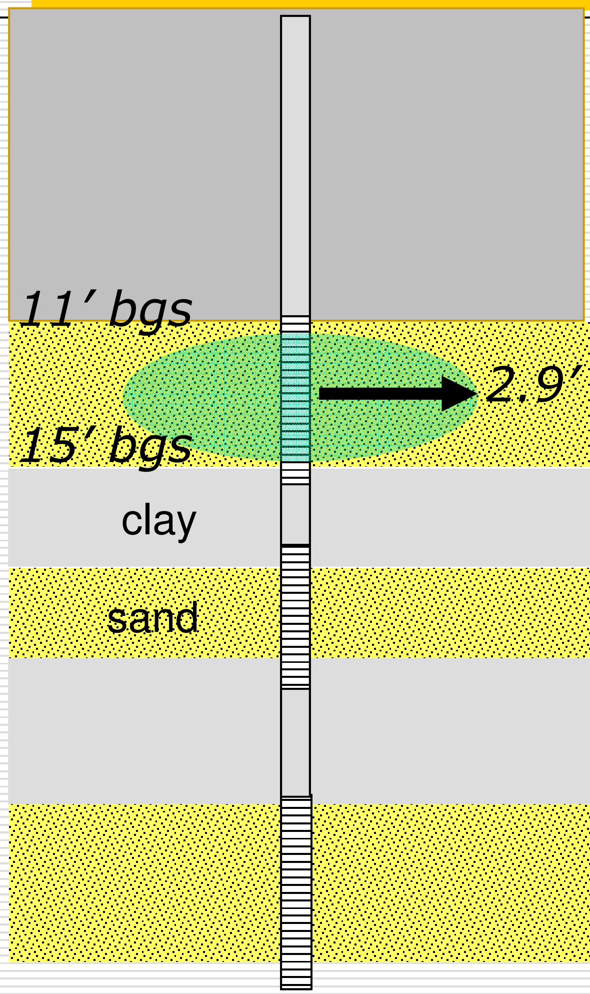
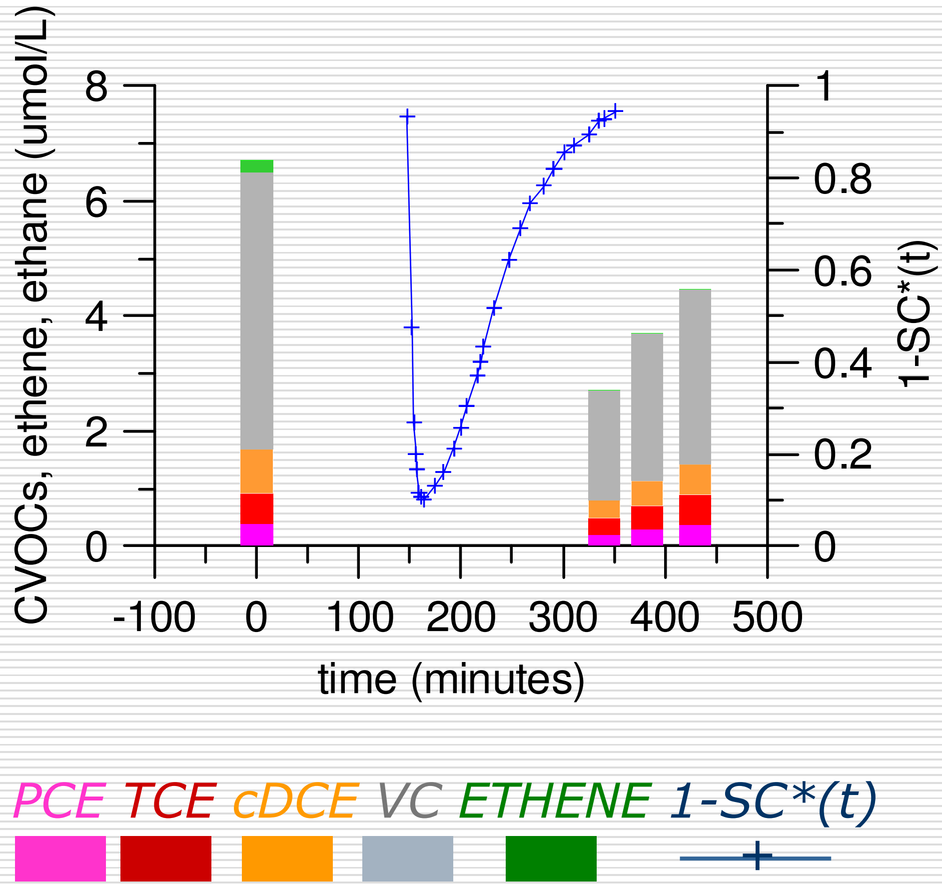
V_{inj} = 699+53 L, V_{ext} = 1,440 L, V_{ext}/V_{inj}=1.9

Push-Pull Test #1

Tap Water Injection

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





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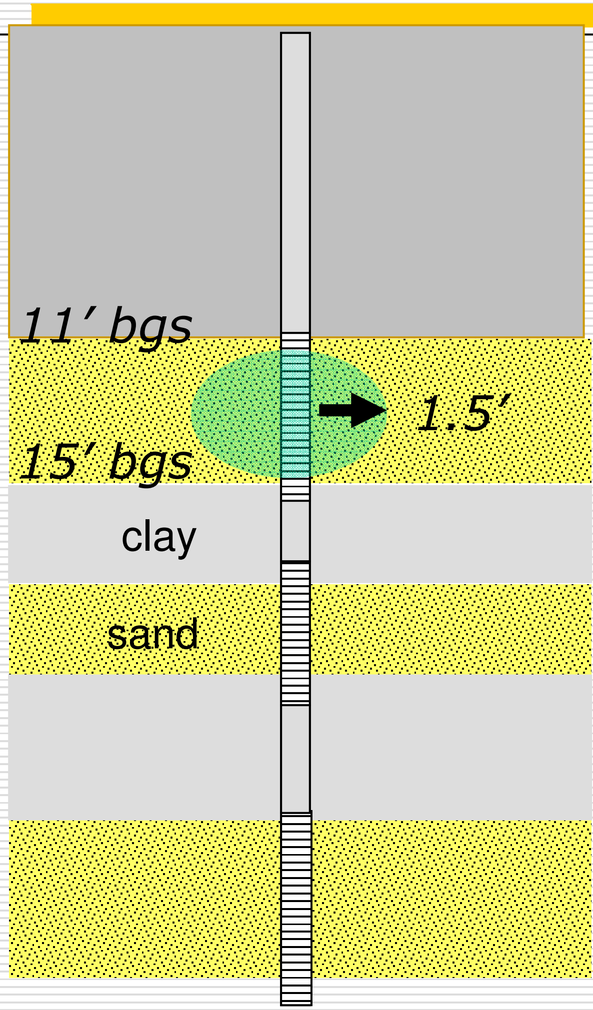
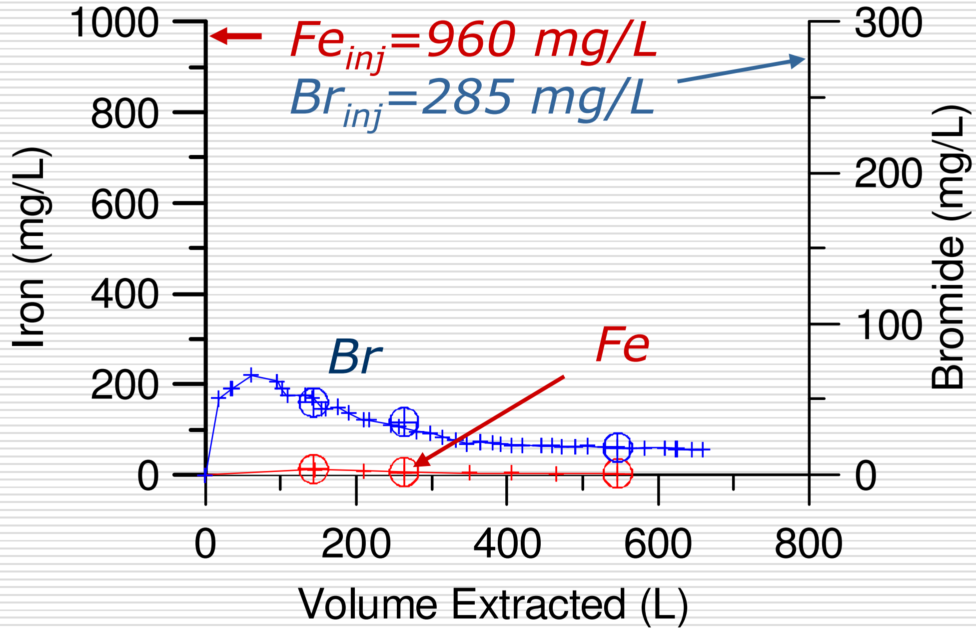
Push-Pull Test #2

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**

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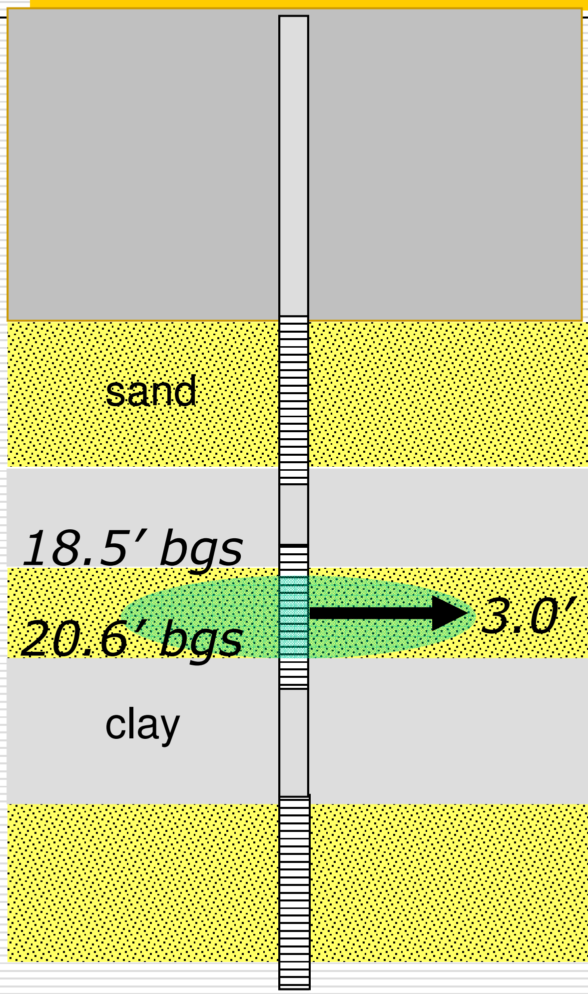
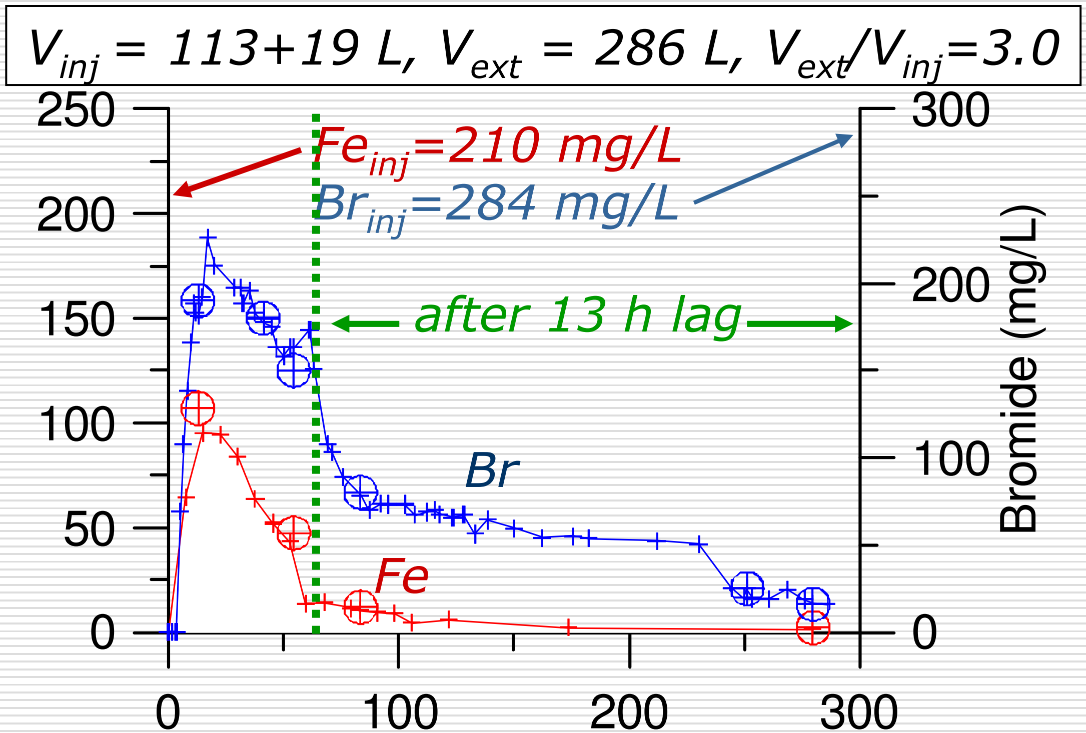
Push-Pull Test #3

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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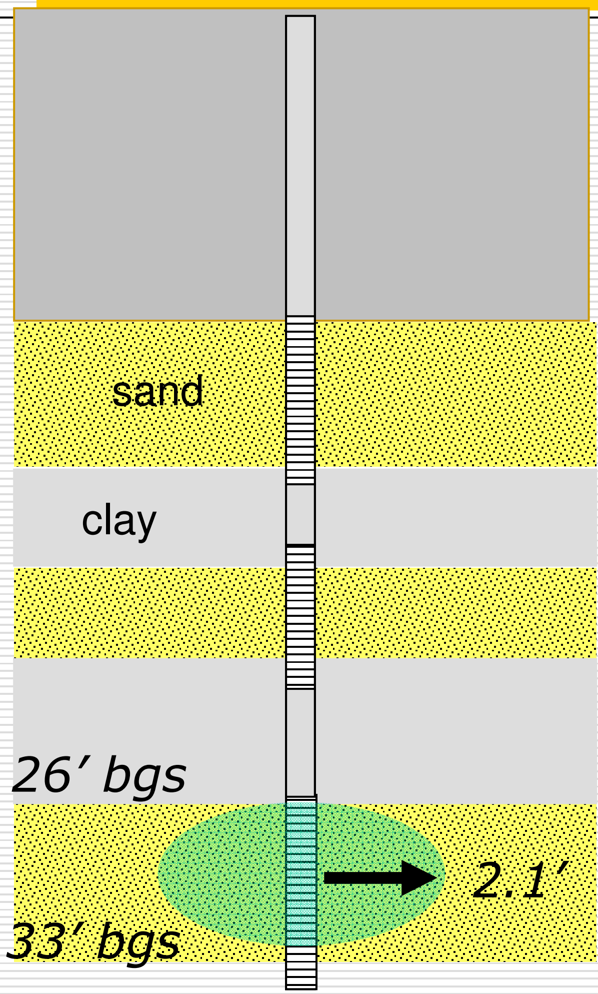
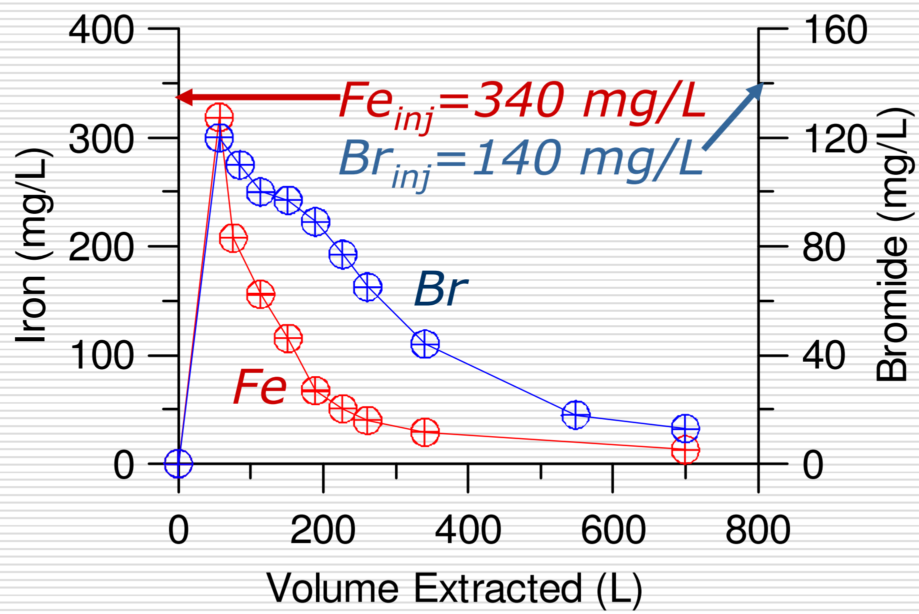
Push-Pull Test #4
nZVI (340 mg/L), no lag time



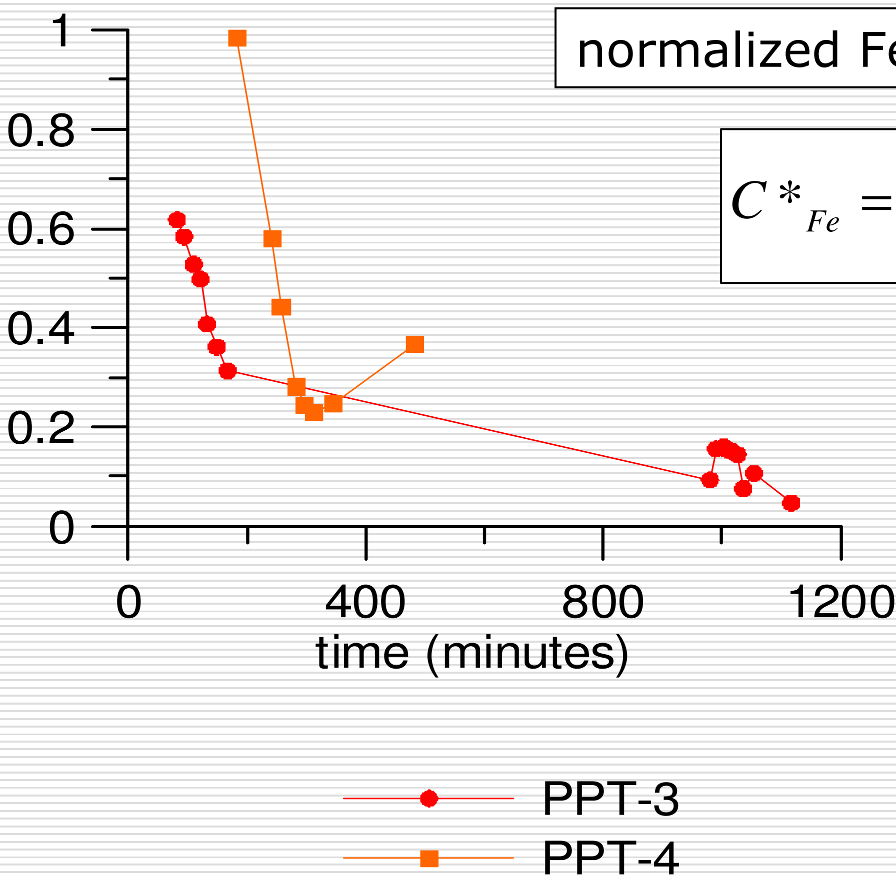
V_{inj} = 329+40 L, V_{ext} = 756 L, V_{ext}/V_{inj}=2.0



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

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.

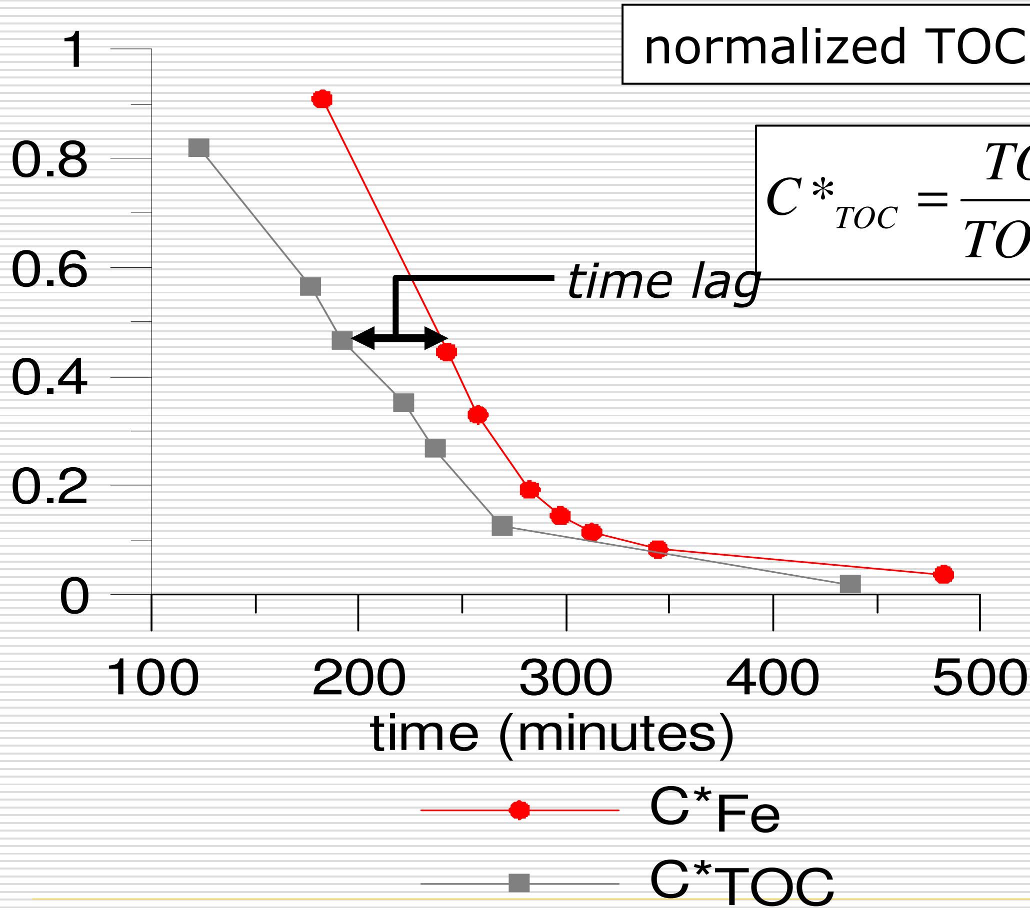
Push-Pull Test#4

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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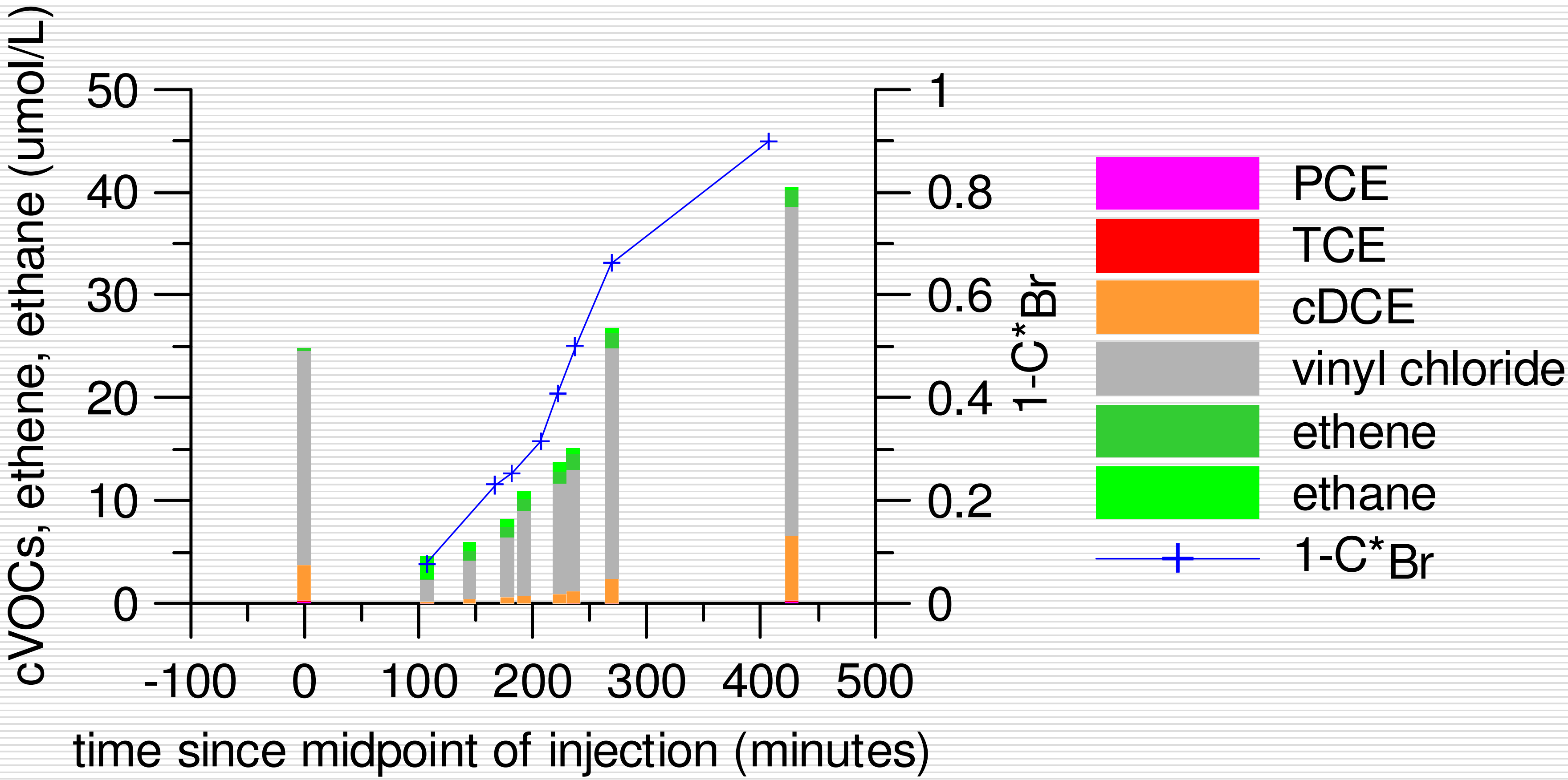
Push-Pull Test #4

Reactivity Assessment



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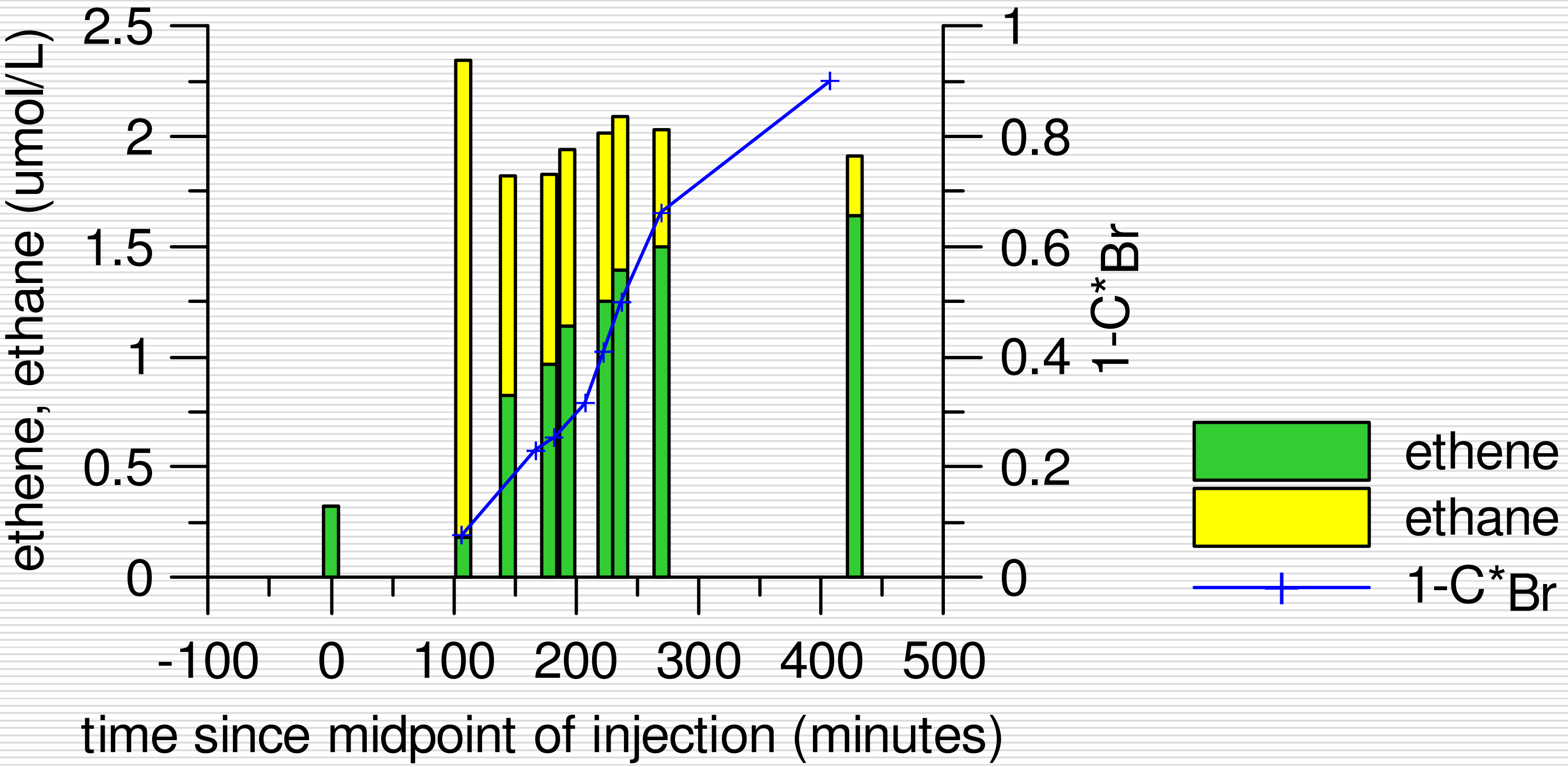
Push-Pull Test #4
Ethane and Ethene Production



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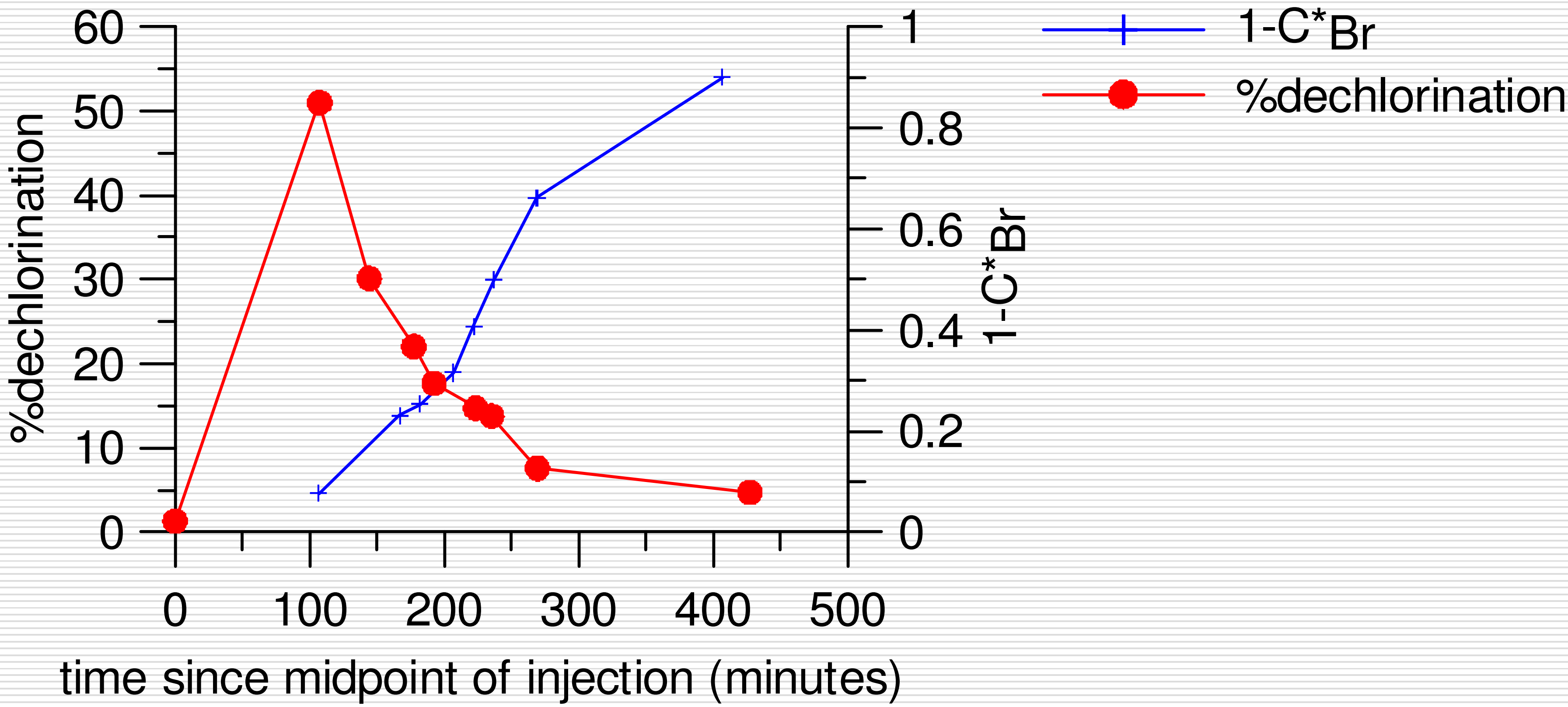
Push-Pull Test #4

%Dechlorination of CVOCs in extracted water samples



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

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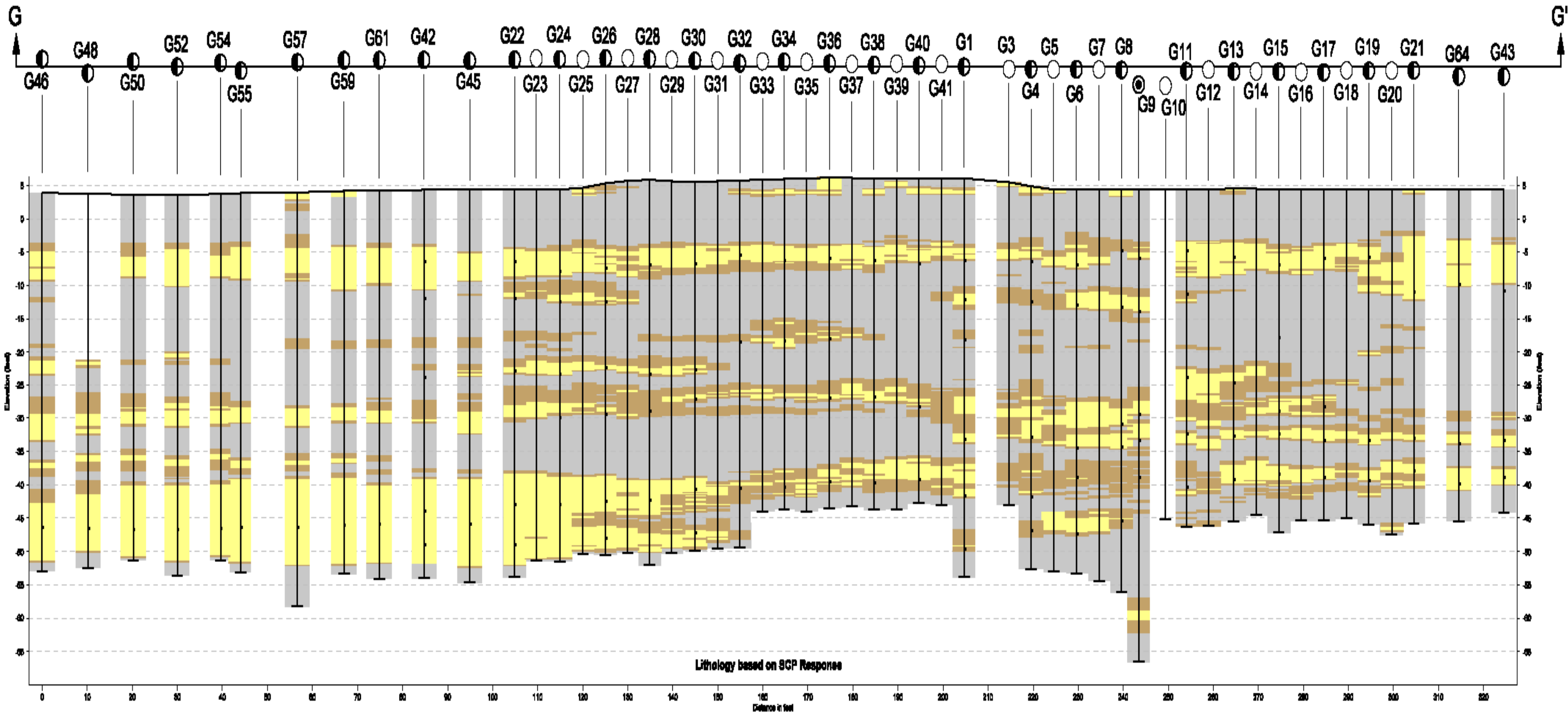
Conclusions

- 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

Cross-section Along Northern Property Boundary



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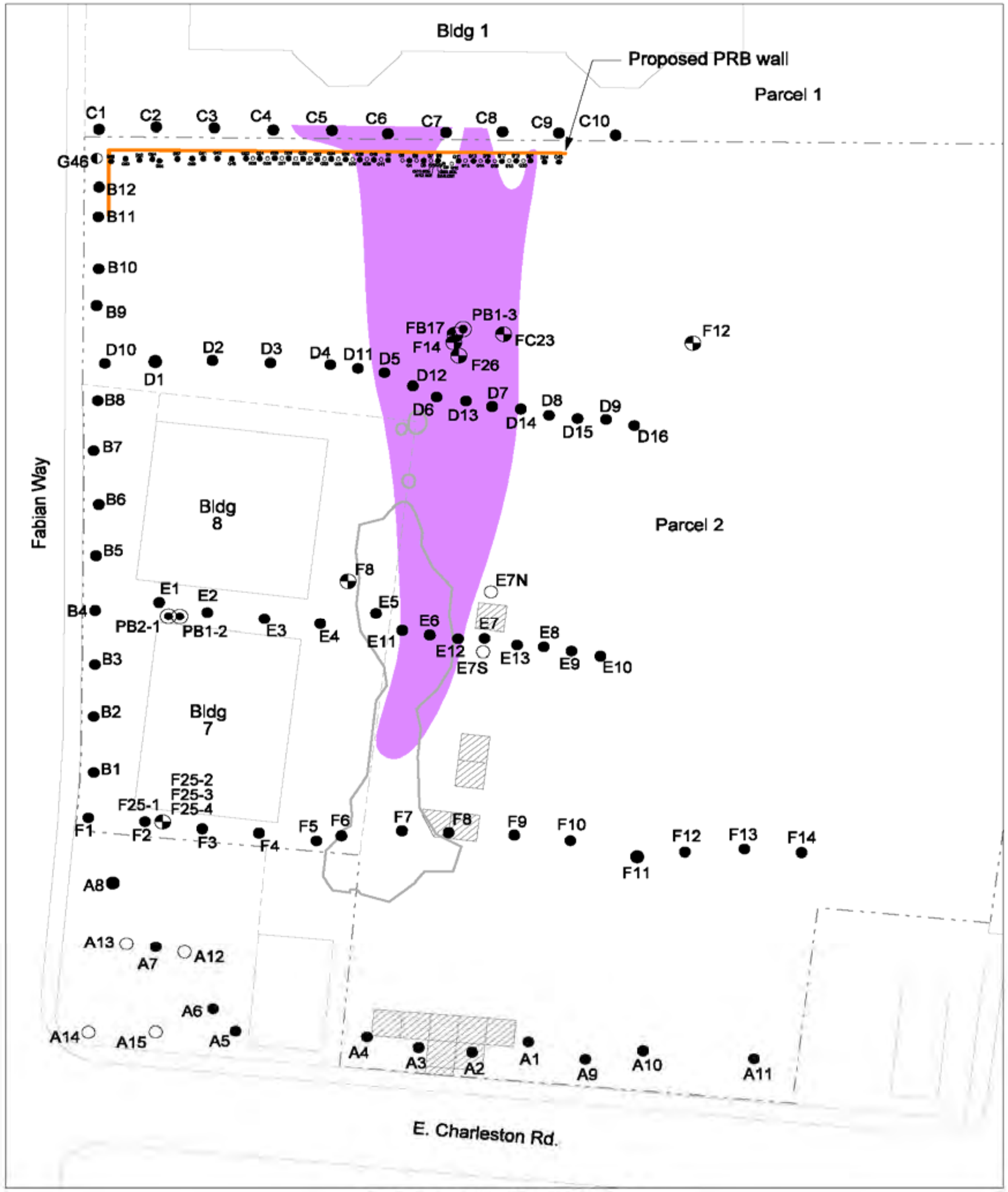
PCE > 100 ppb

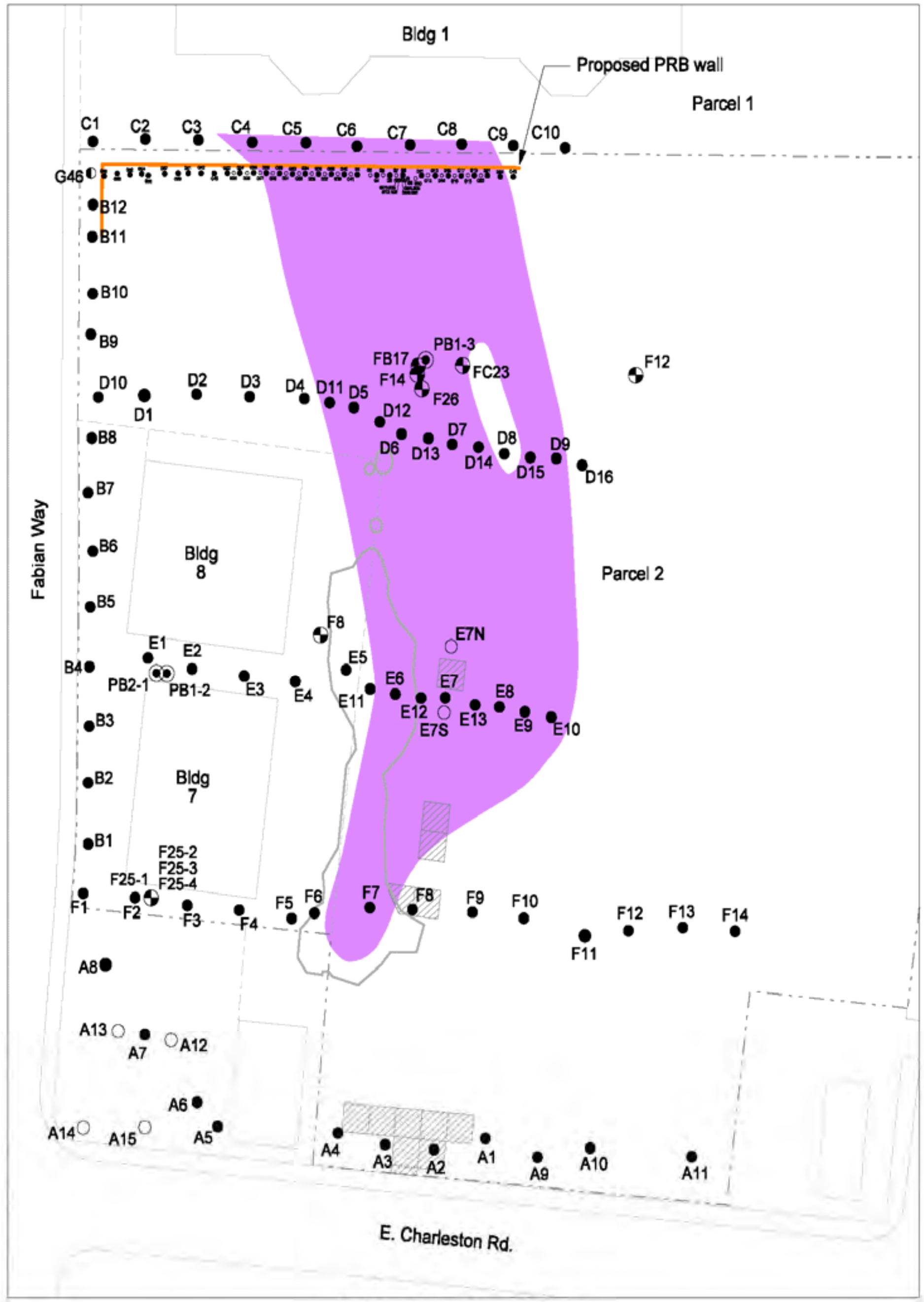
8 to 15 feet bgs



8-15 Feet Below Ground Surface

PCE > 100 ppb

15 to 40 feet bgs



15-40 Feet Below Ground Surface

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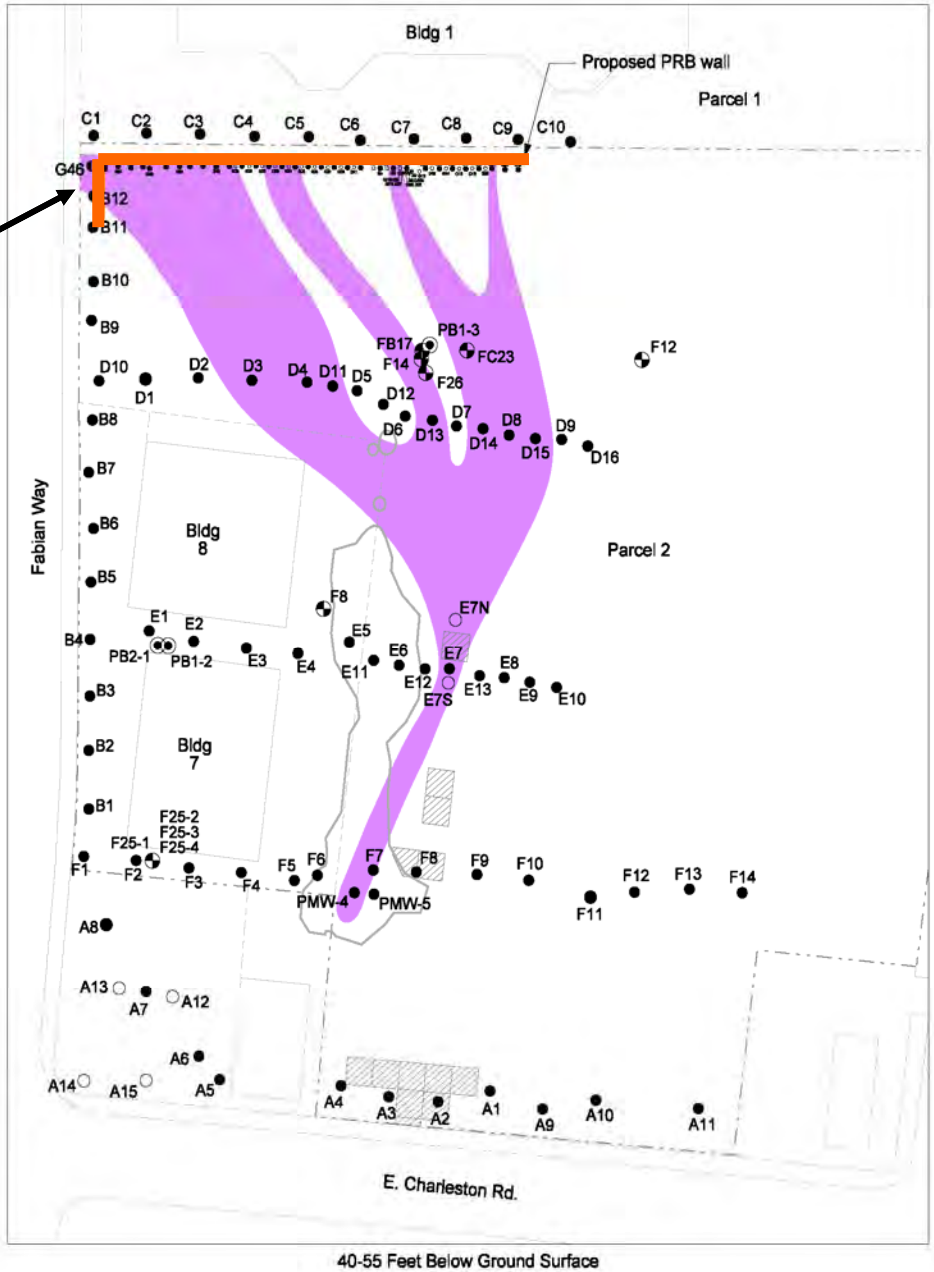
PRB

PCE > 100 ppb

40 to 55 feet bgs



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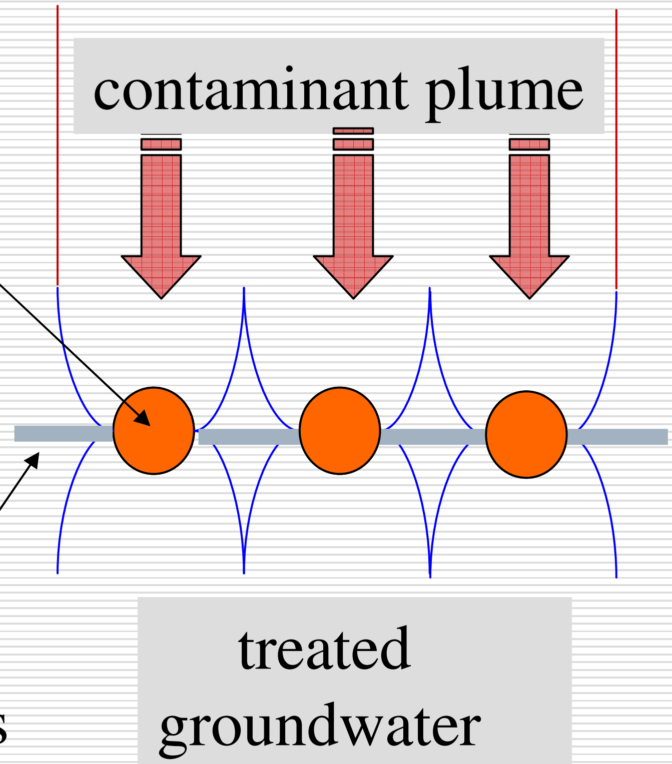
Design Challenges

- 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

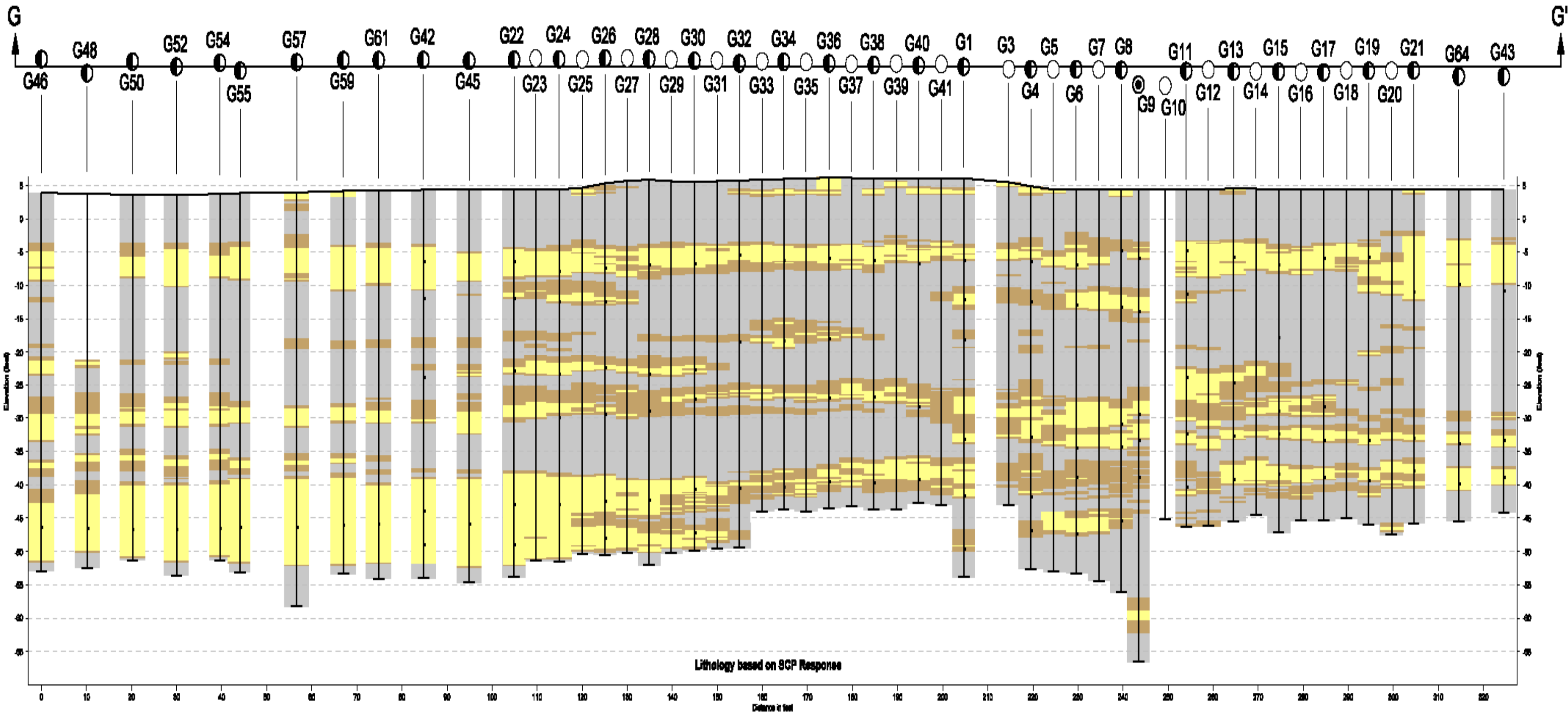
ZVI gates
3 ft diameter multi-layered caissons



Slurry wall funnels
370 ft long continuous slurry wall

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

Cross-section Along PRB



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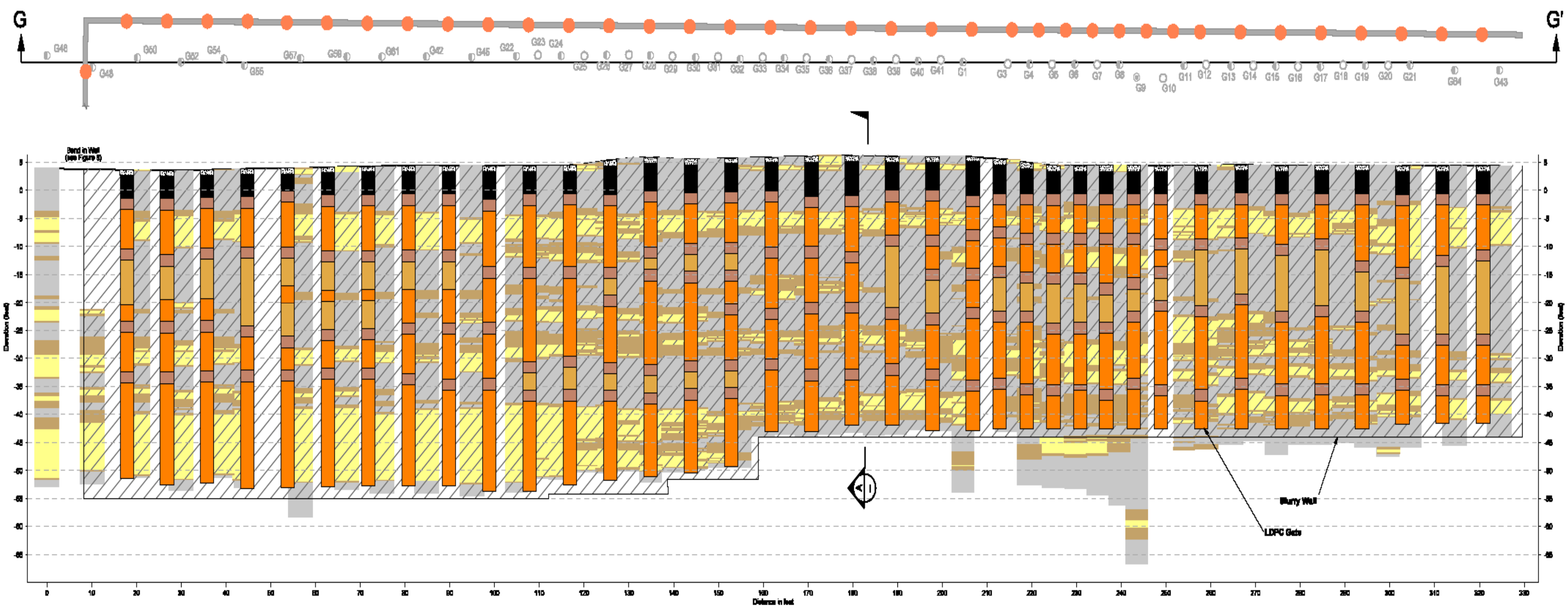
PRB Design



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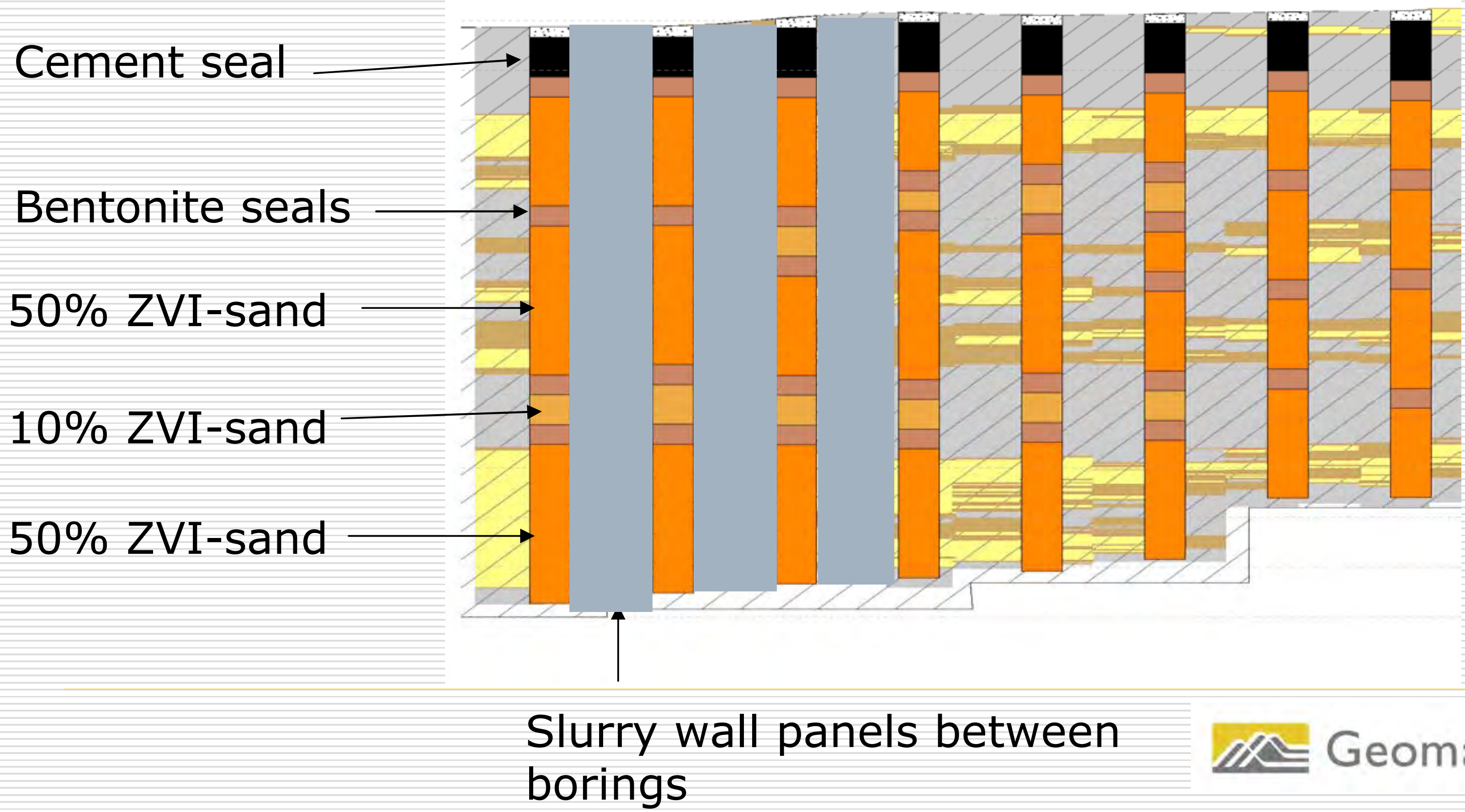
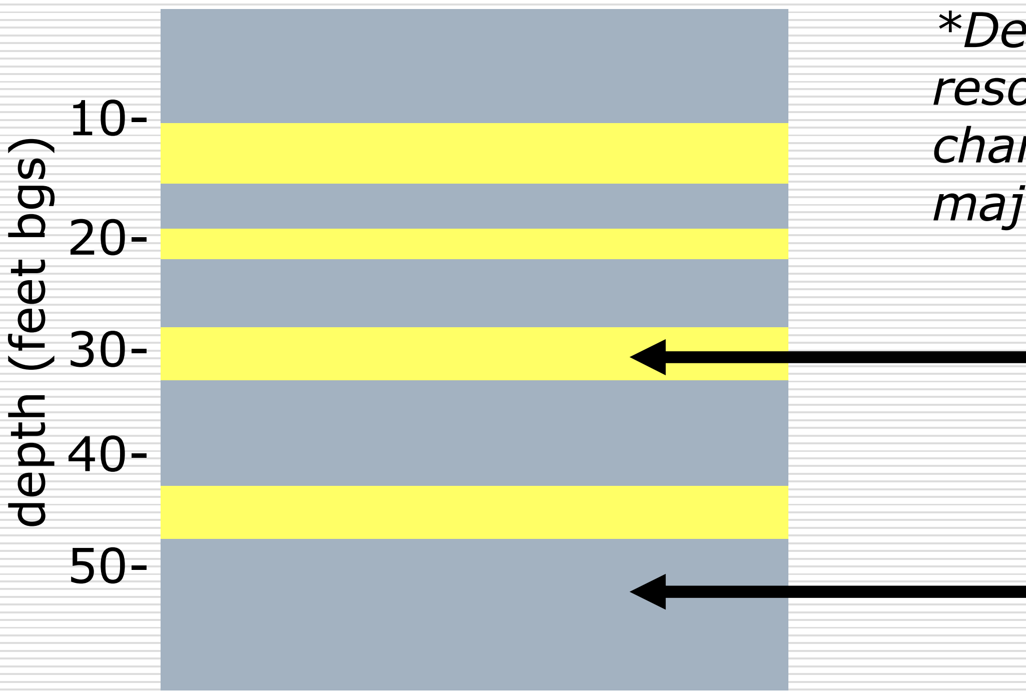
PRB Design


Cement seal
Bentonite seals
50% ZVI-sand
10% ZVI-sand
50% ZVI-sand
Slurry wall panels between borings

Construction Methods – Step 1

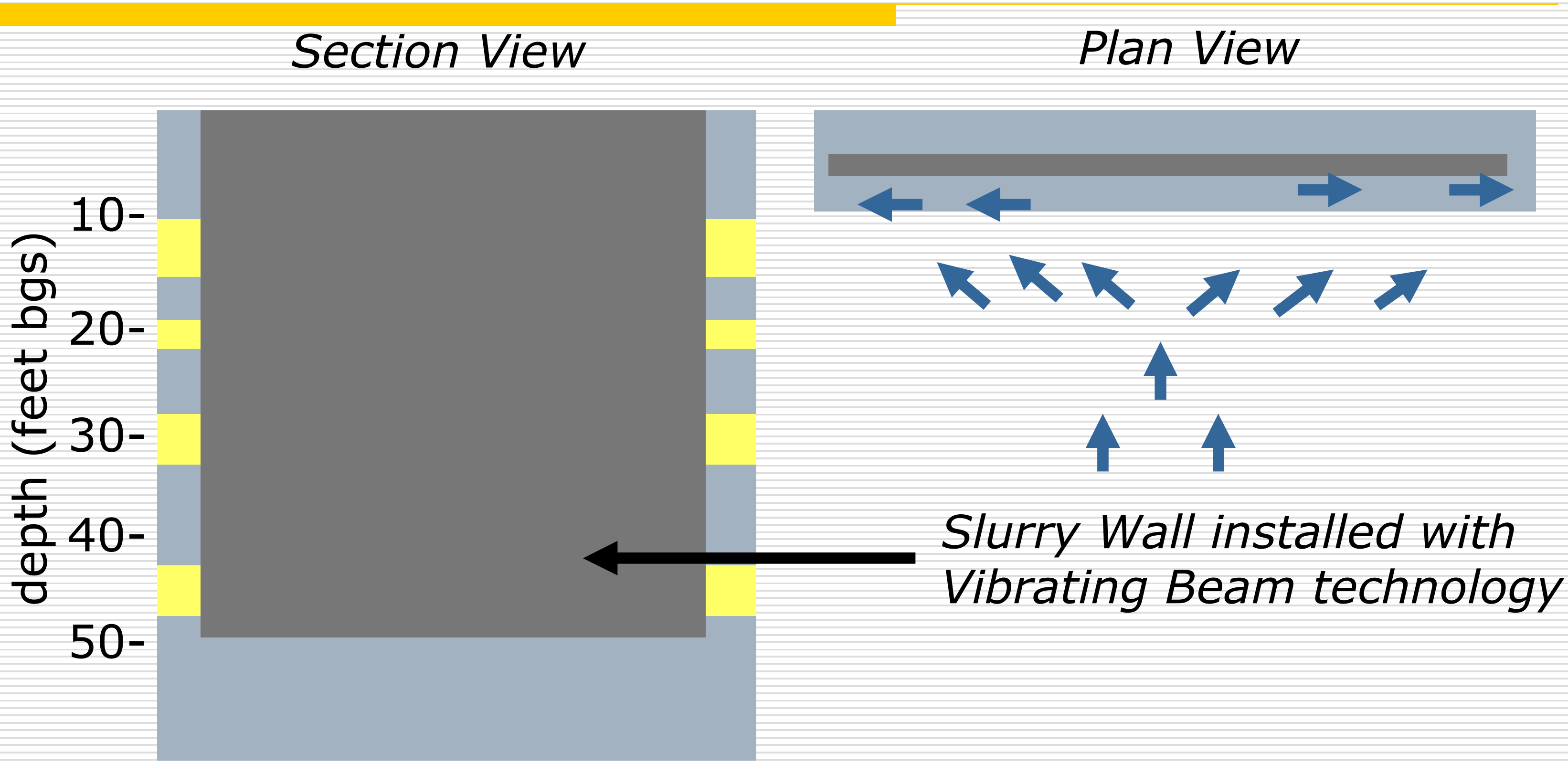
**Design based on high resolution lithologic characterization to identify major water-bearing zones*



coarse-grained (WBZ)

silty clay (aquitard)

Construction Methods – Step 2



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

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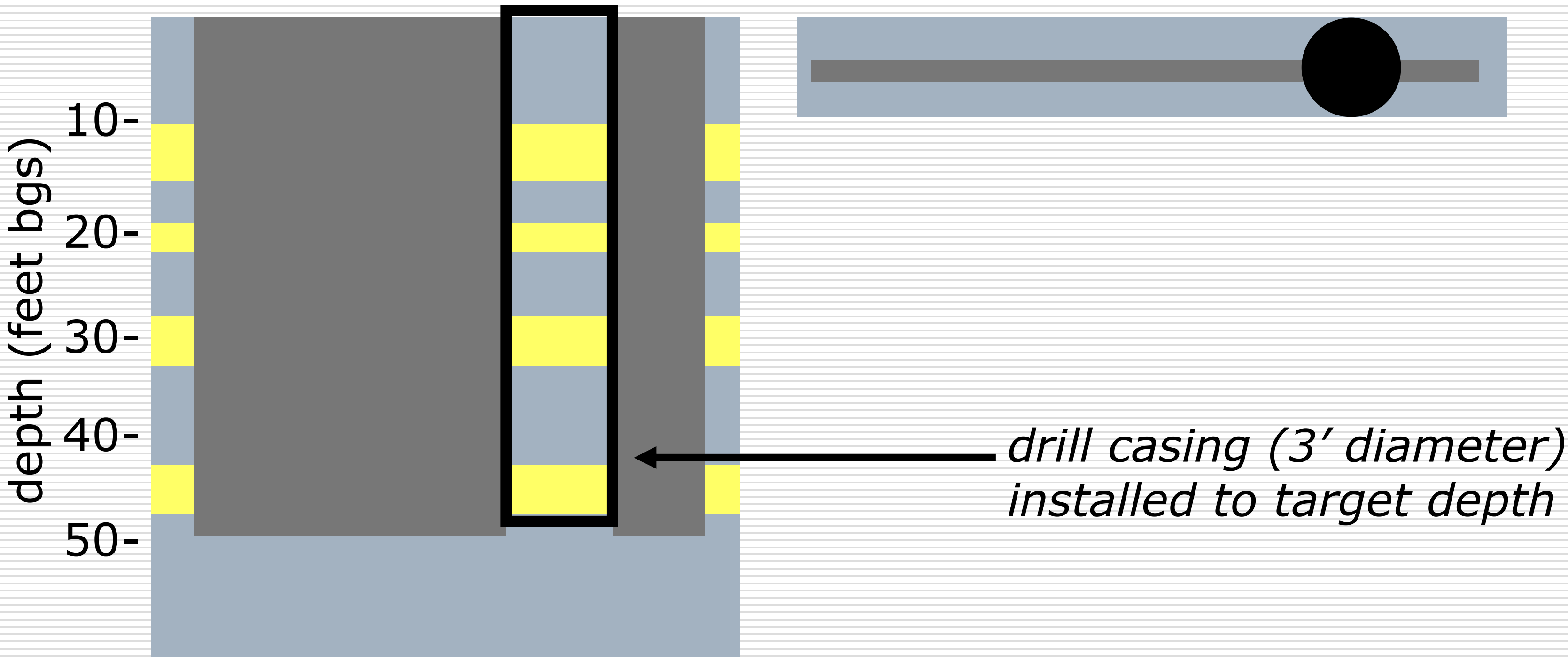
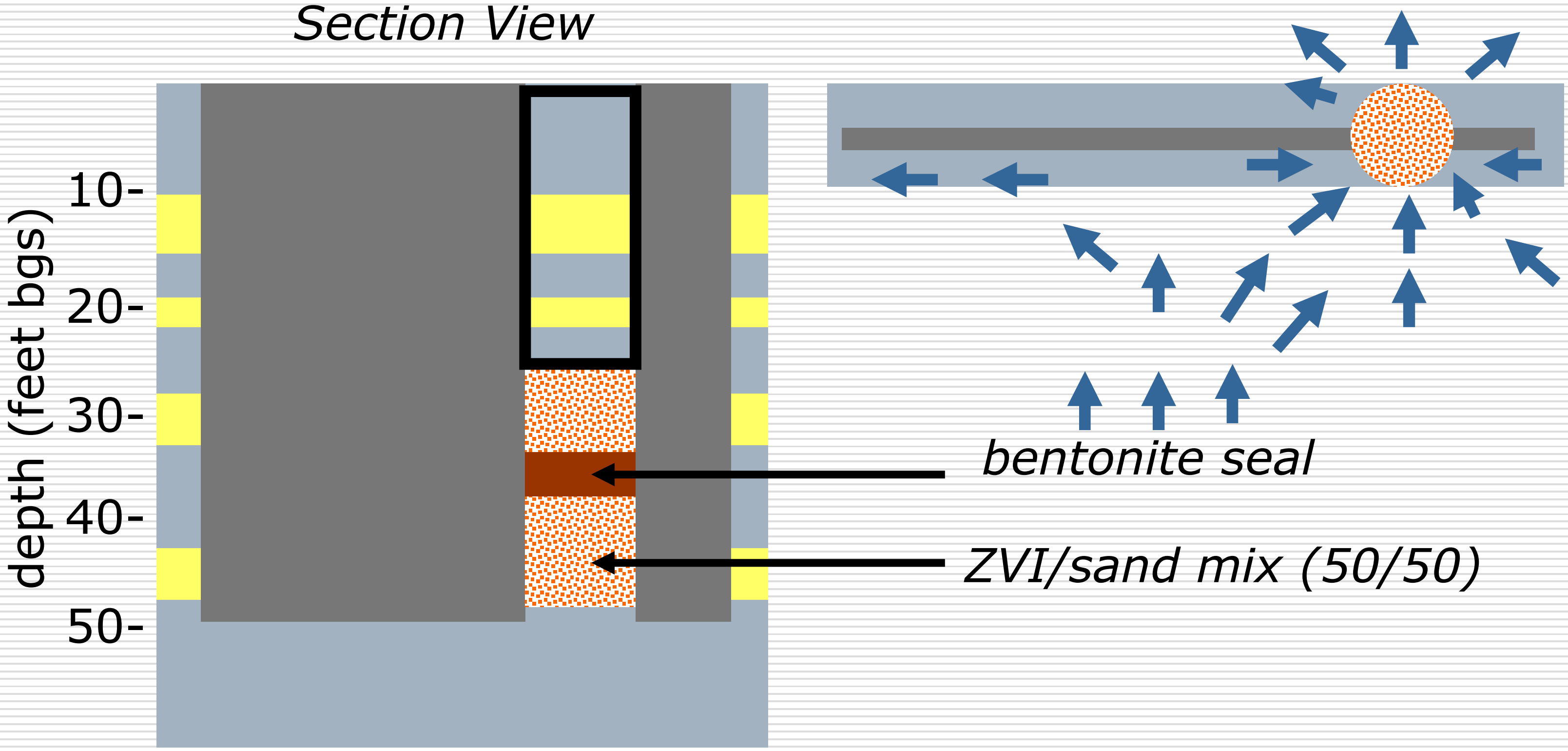
Construction Methods – Step 3



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

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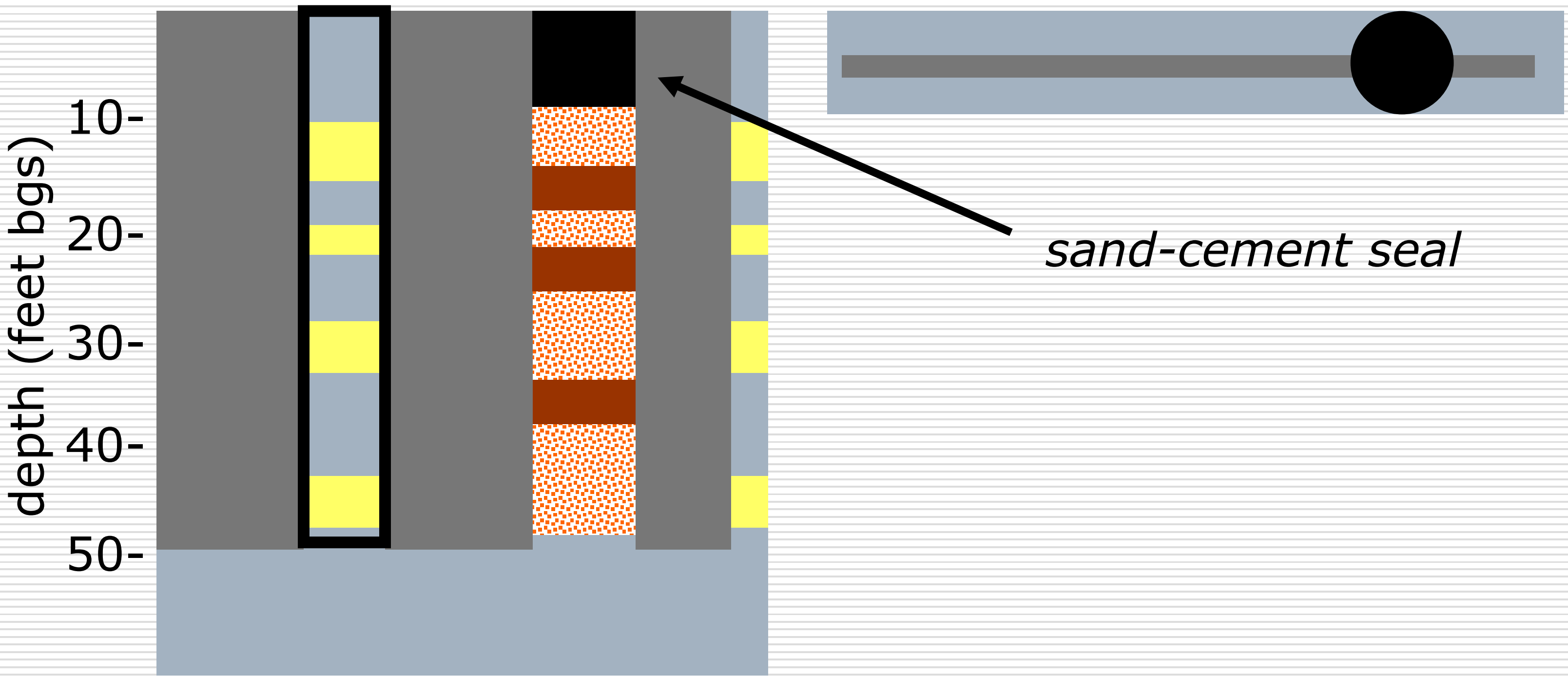
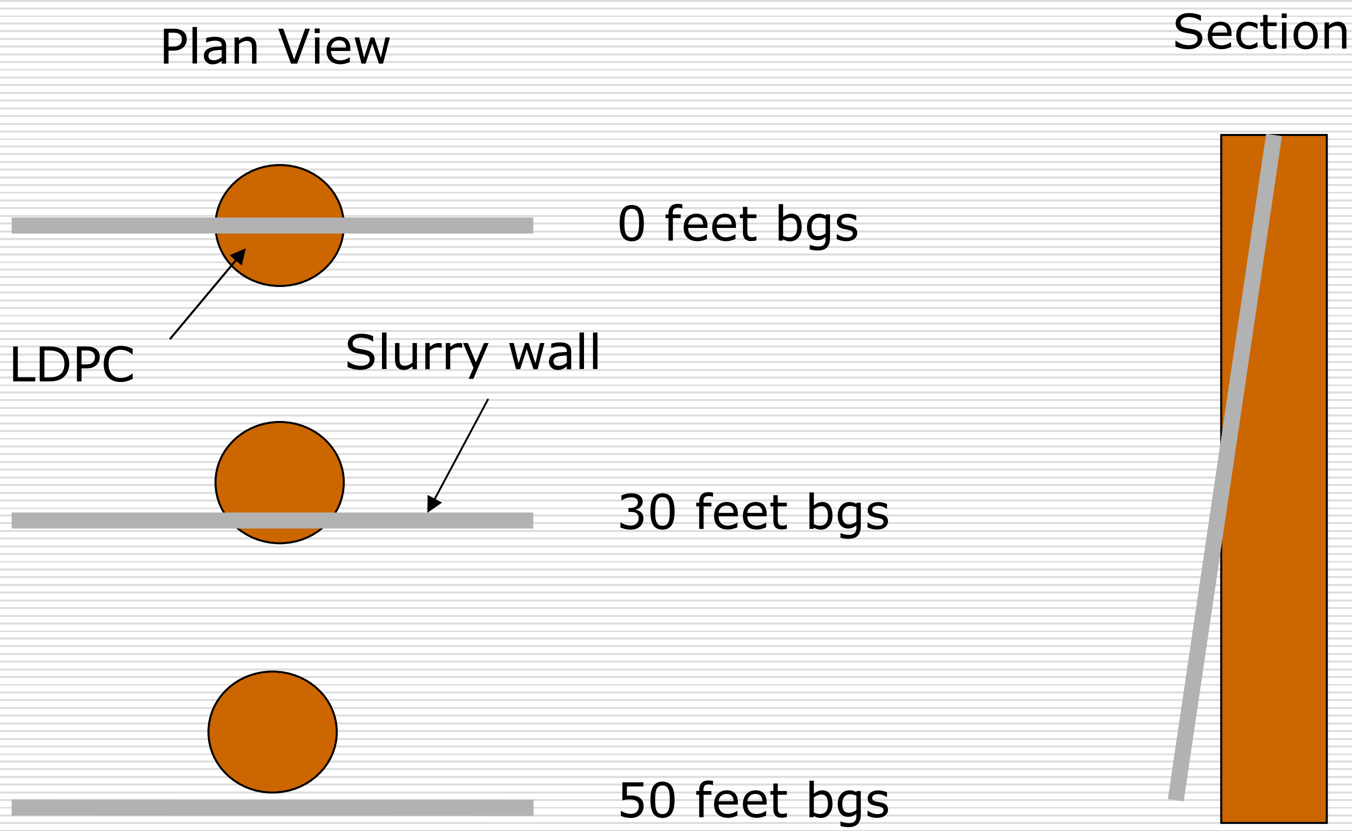
Construction Methods – Step 5



Drilling of adjacent boring

Possible Deviation Issues



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Slurry
Systems

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REIMER
Quick Mix Concrete
650-326-3030
CA 180301
54

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Construction Summary

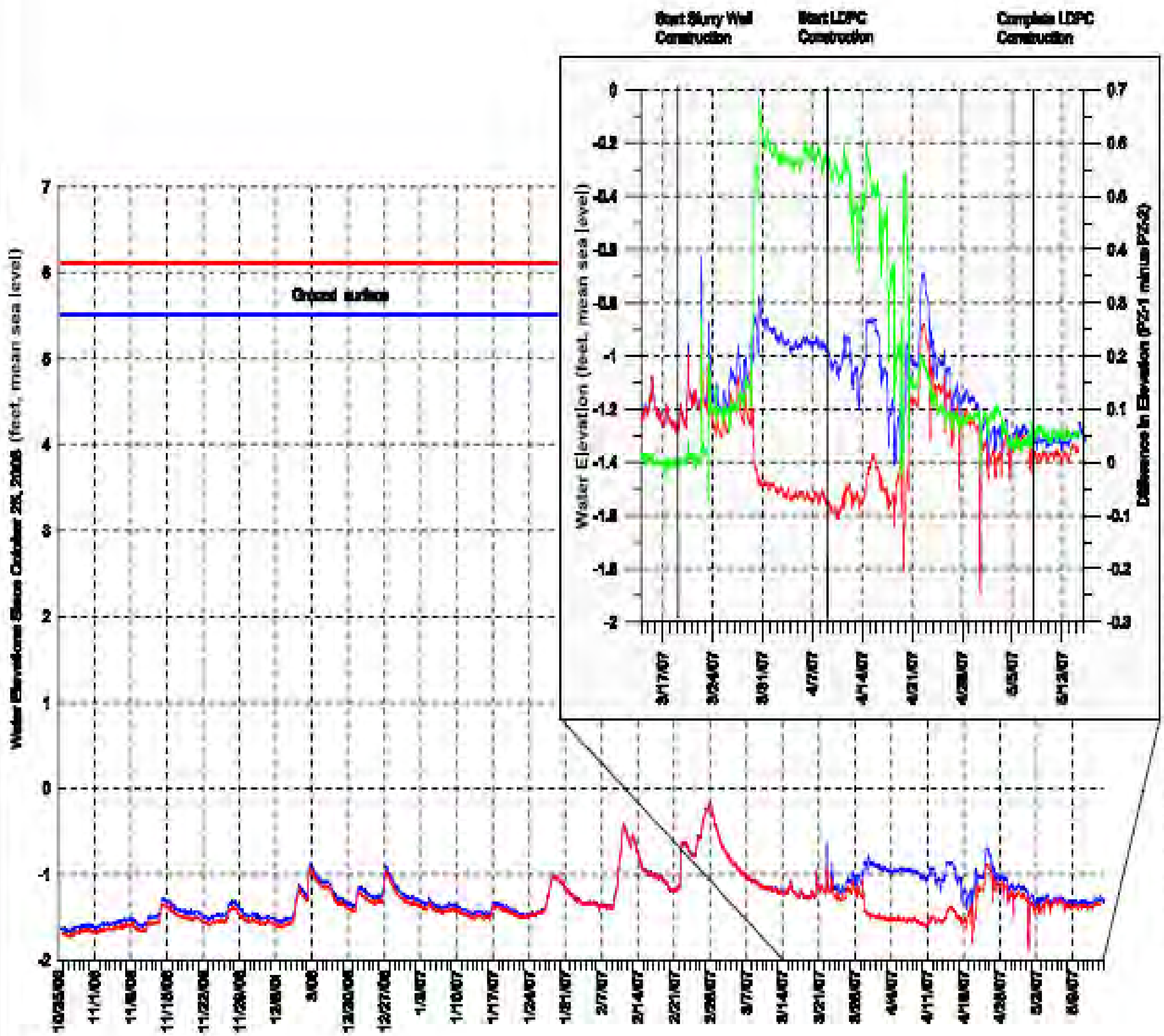
GENERAL	
Construction period	56 days
VIBRATING BEAM BARRIER WALL	
Total length	371 feet
Maximum depth	60 feet
Minimum depth	48.5 feet
Total square feet of wall	20,480 square feet
Slurry produced	13,699 cubic feet
Excess slurry disposed off-site	6,460 cubic feet
Average thickness of slurry wall[3]	5.8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

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	0.56
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.

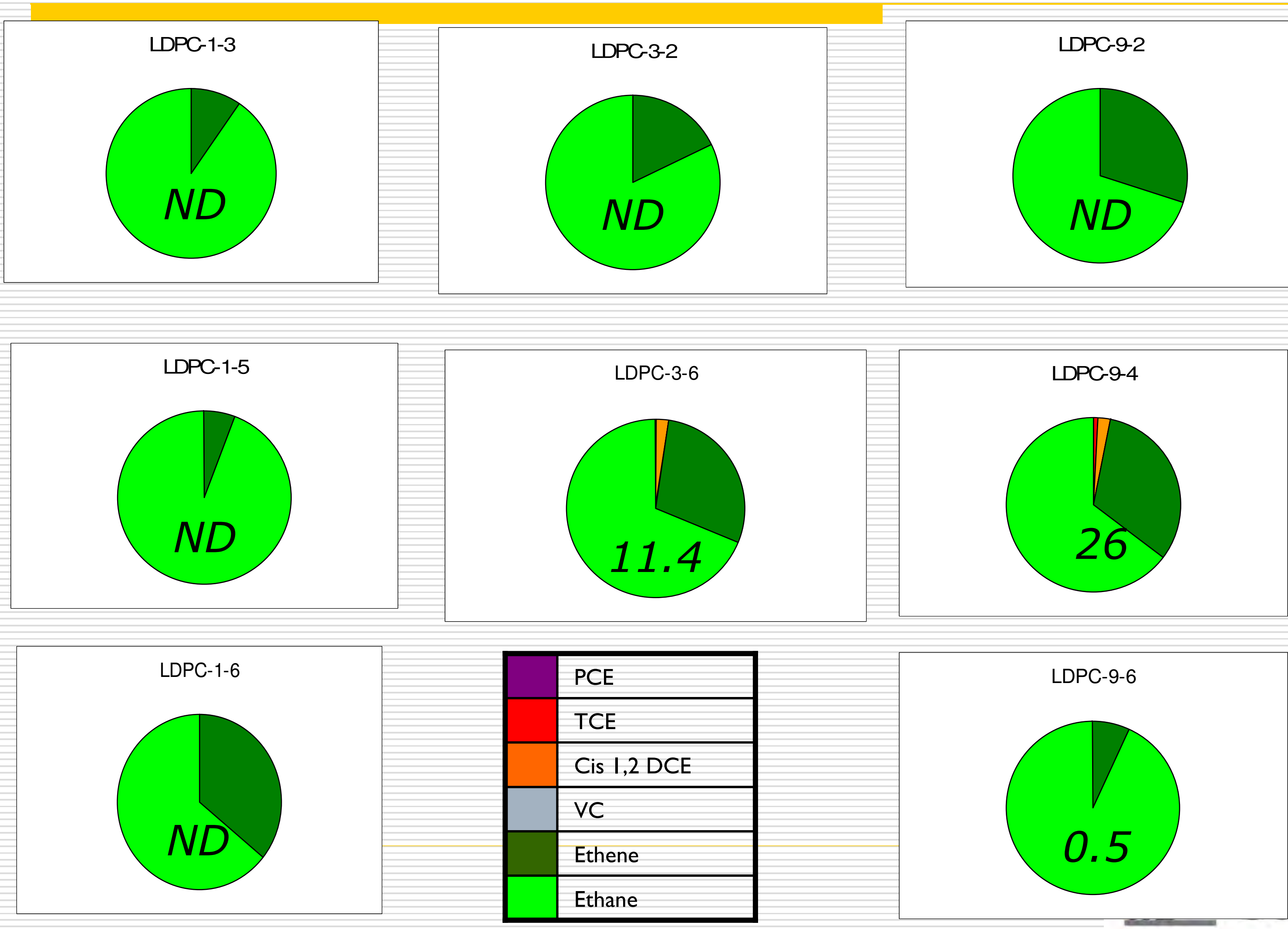
WATER LEVEL ELEVATIONS
PZ-1 AND PZ-2
901 San Antonio Road, Parcel 2
Palo Alto, California

By: MC	Date: 08/20/07	Project No. 9311.005

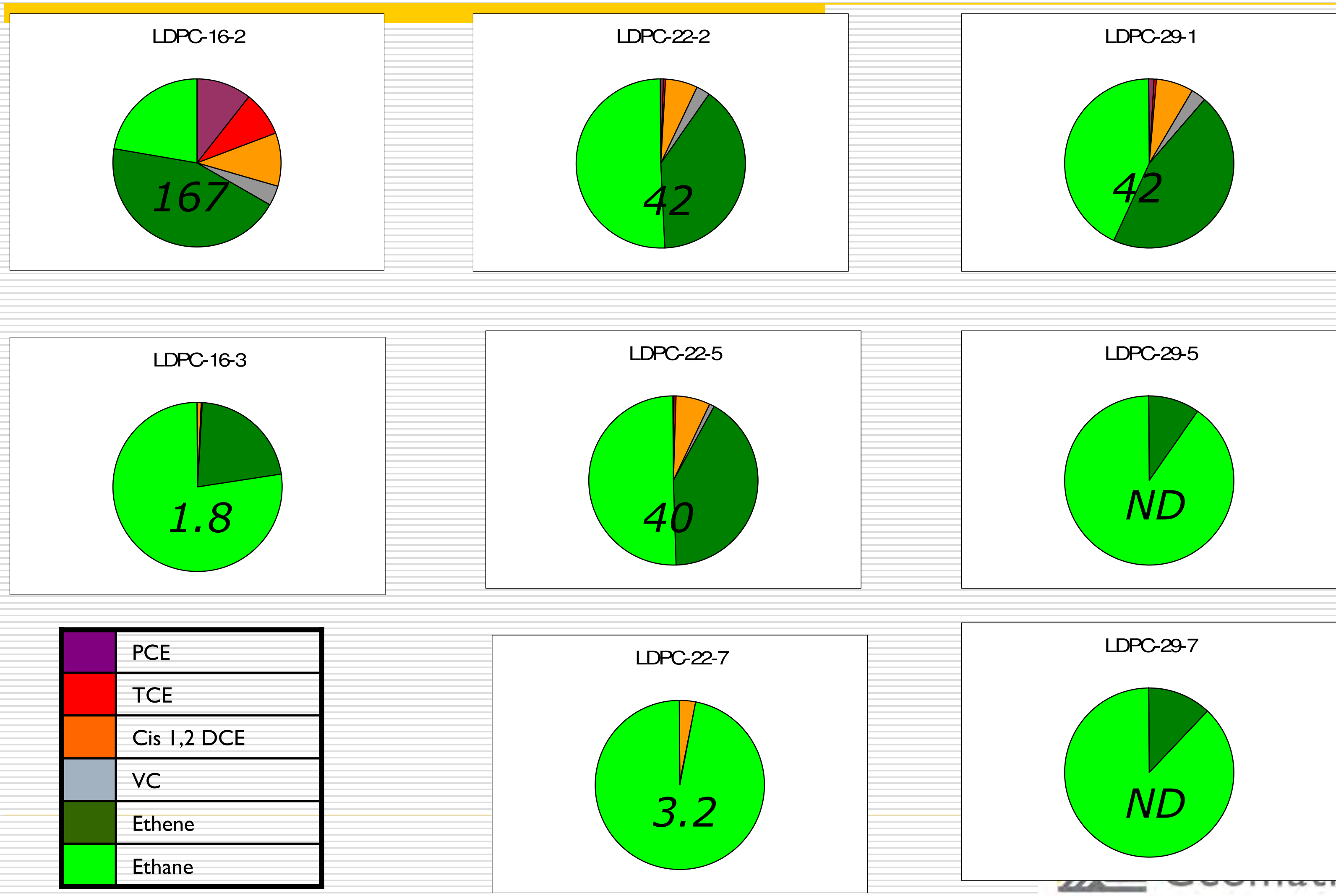
Geomatrix

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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