



Use of Nano- and Micro-Scale Zero Valent Iron at Navy Sites: A Case Study

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US EPA Workshop on Nanotechnology for Site Remediation

Washington, DC

October 2005

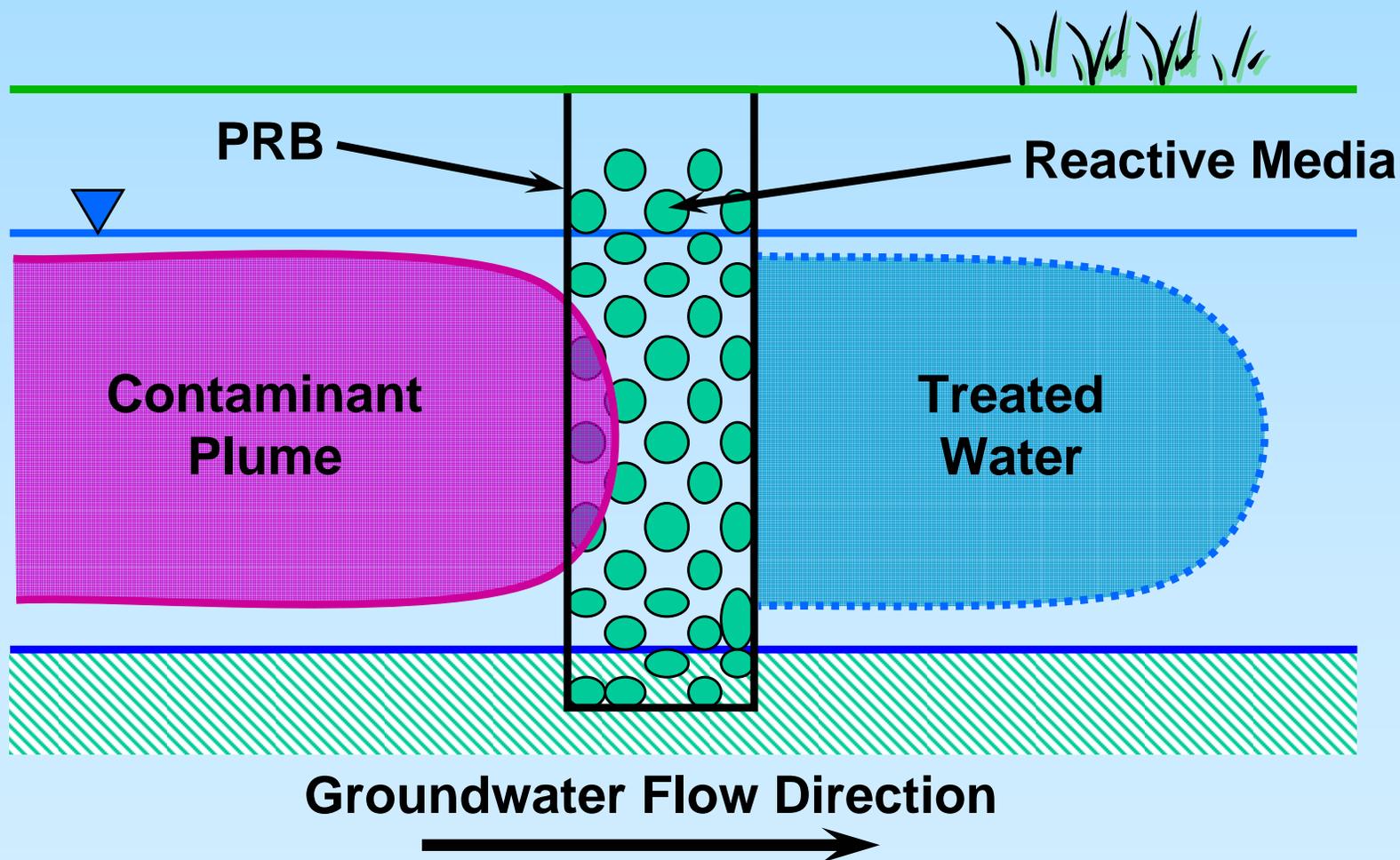
- Introduction
- Case Studies
- Cost Analysis
- Summary of Conclusions



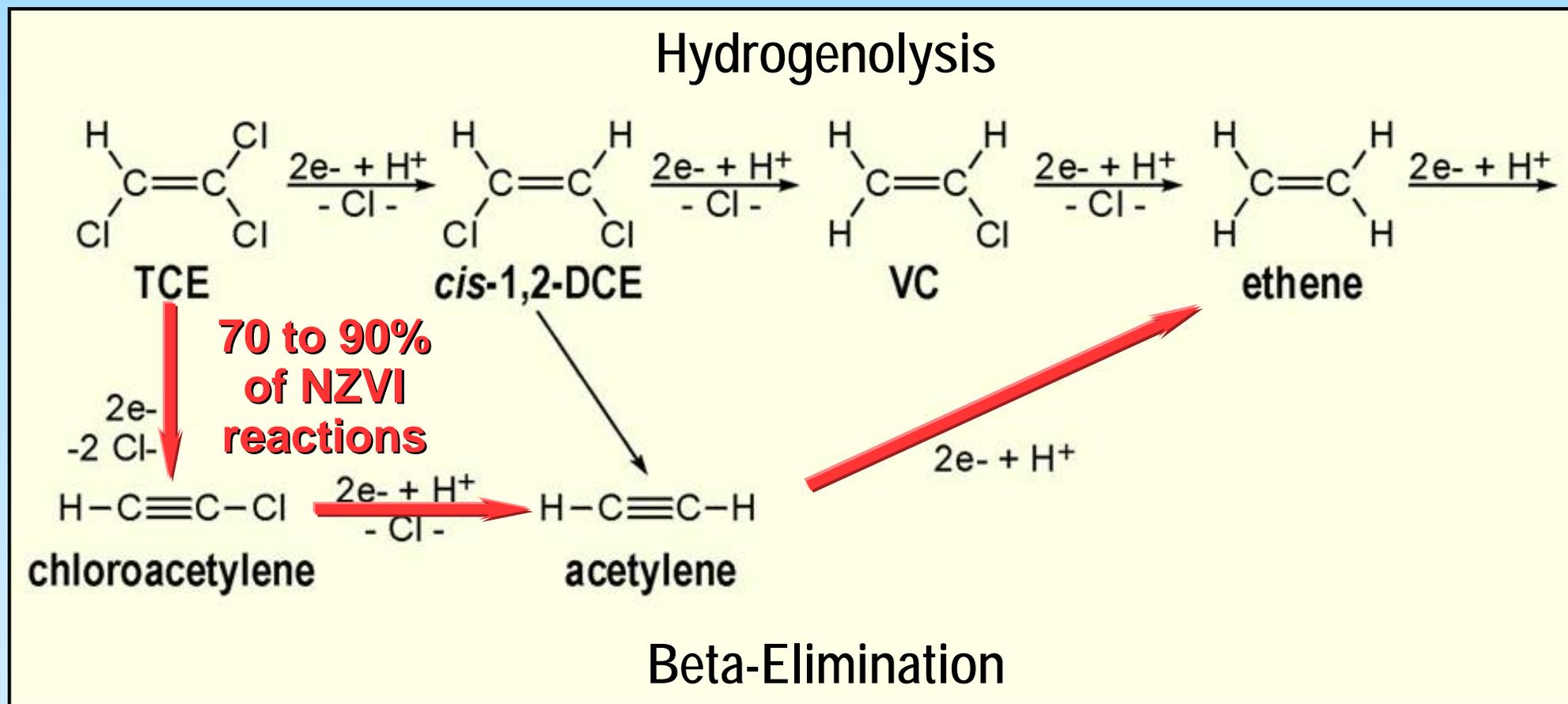
Use of ZVI in Permeable Reactive Barriers (PRBs)



**Passive Treatment,
No Aboveground Structures**



Multiple Pathways for TCE Degradation



NZVI in Hydraulic Fracture



- Introduction

- Case Studies

- Naval Air Station, Jacksonville, FL
- Hunters Point Shipyard, San Francisco, CA
- Naval Air Engineering Station, Lakehurst, NJ

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Case Study 1: Naval Air Station Jacksonville, FL



- Site History
- Site Conditions
 - Contaminant Levels
 - Contaminant Extent
- Technology Implementation
- Results
- Conclusions/Lessons Learned

Site History – NAS Jacksonville, Hangar 1000



- In operation since 1940
- Former USTs, Tanks A and B
 - Waste solvents
 - USTs removed in 1994
 - Primary source appears to be Tank A
- Source area contains TCE, PCE, 1,1,1-TCA, and 1,2-DCE
 - Cleanup managed under CERCLA
 - Groundwater monitoring under RCRA

Site Conditions – Contaminant Levels



CVOC mass estimates 42 to 125 lb

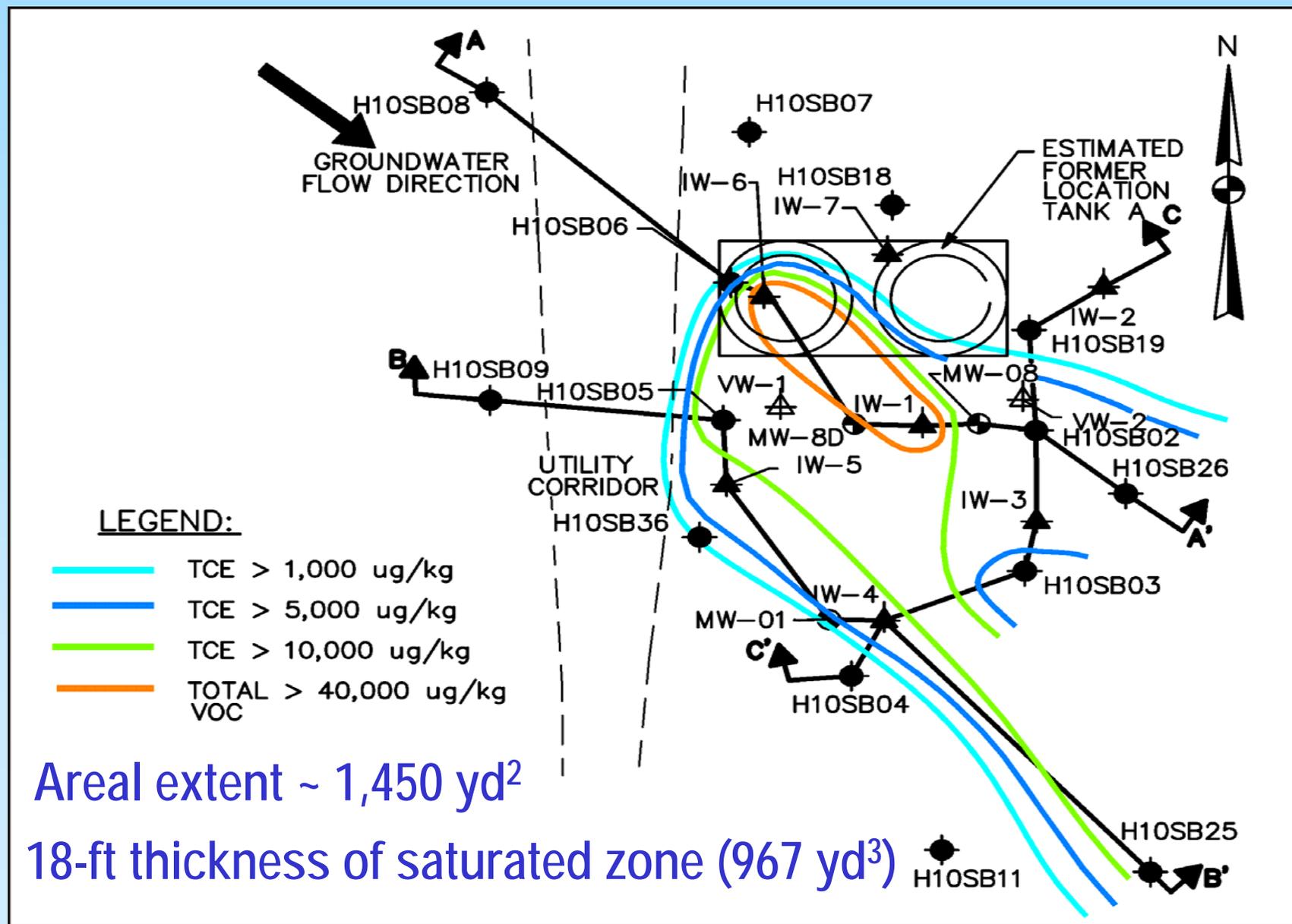
Max soil concentrations:

- PCE – 4,360 $\mu\text{g}/\text{kg}$
- TCE – 60,100 $\mu\text{g}/\text{kg}$
- 1,1,1-TCA – 25,300 $\mu\text{g}/\text{kg}$

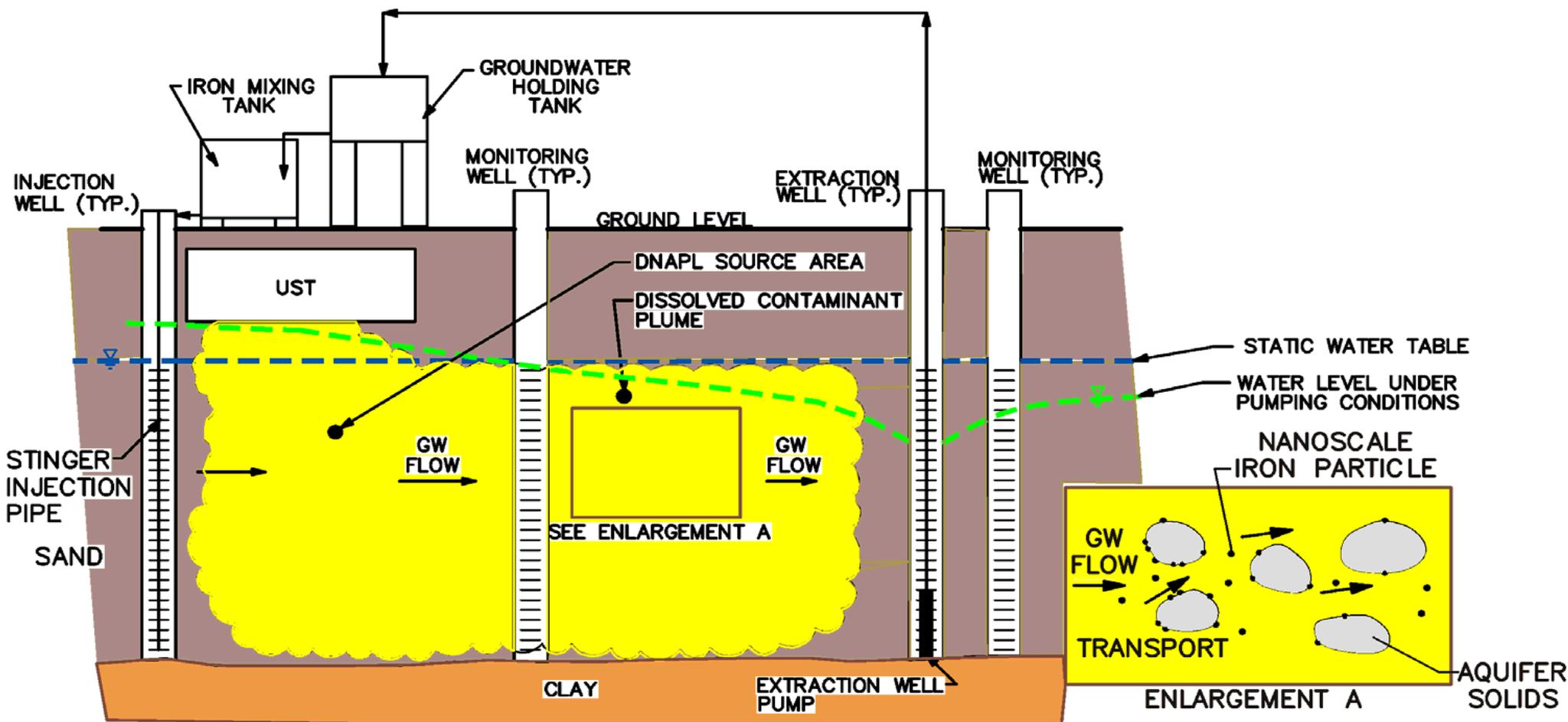
Max groundwater concentrations (baseline):

- PCE – 210 $\mu\text{g}/\text{L}$
- TCE – 26,000 $\mu\text{g}/\text{L}$
- 1,1,1-TCA – 8,400 $\mu\text{g}/\text{L}$
- *cis*-1,2-DCE – 6,700 $\mu\text{g}/\text{L}$

Extent of Contamination



Technology Implementation



300 lb BNP (99.9 % Fe, 0.1 % Pd and polymer support)

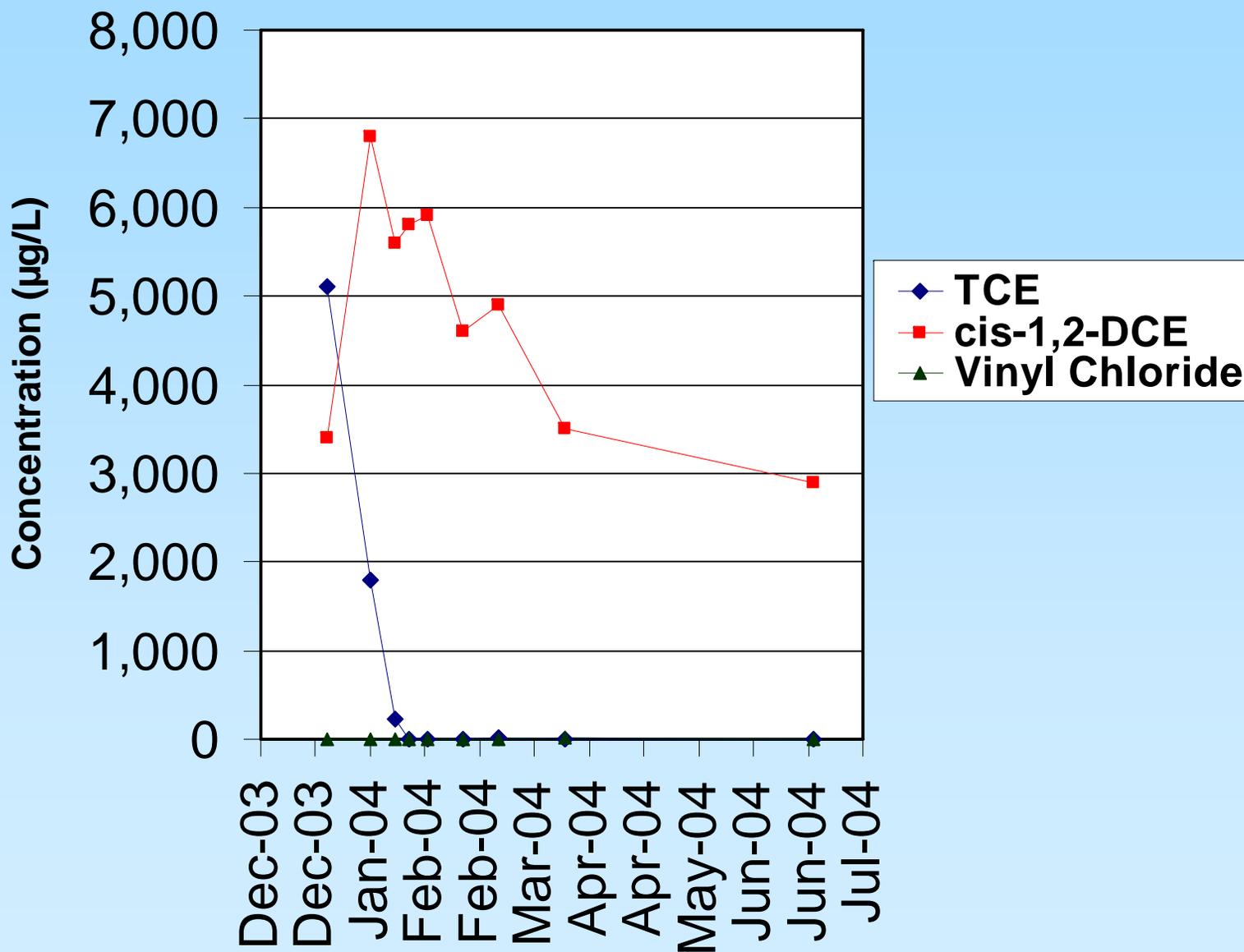
Gravity Feed, 10 injection points

Results – Technology Performance Evaluation



- Good reduction in dissolved TCE levels
- Nitrate, sulfate reduction
- Ethene, ethane formation
- Significant increase in DCE levels, indicating biodegradation
- Not observed (signs of strong enough reducing conditions to generate abiotic reduction)
 - ORP levels well below -200 mV (-400 to -750 mV common in iron barriers)
 - pH of 8 or higher (pH of 10 or 11 observed in iron barriers)
 - Decrease in alkalinity, Ca, Mg

Concentrations in Source Zone Well H10MW37



Conclusions/Lessons Learned



- NZVI significantly reduced dissolved TCE levels
- Avoid NZVI contact with oxygen (or other oxidized species) during storage or mixing to avoid deactivation
- Determine Fe mass based on Fe/groundwater ratio, rather than Fe/Contaminant ratio
 - ORP < -200 mV required in target treatment volume
- Identify and address long-term performance goals

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Case Study 2: Hunters Point Shipyard



Site RU-C4 – Parcel C (San Francisco, CA)

- Site History
- Site Conditions
 - Contaminant Levels/Extent
 - Hydrogeologic Conditions
- Technology Implementation
- Results
- Conclusions/Lessons Learned

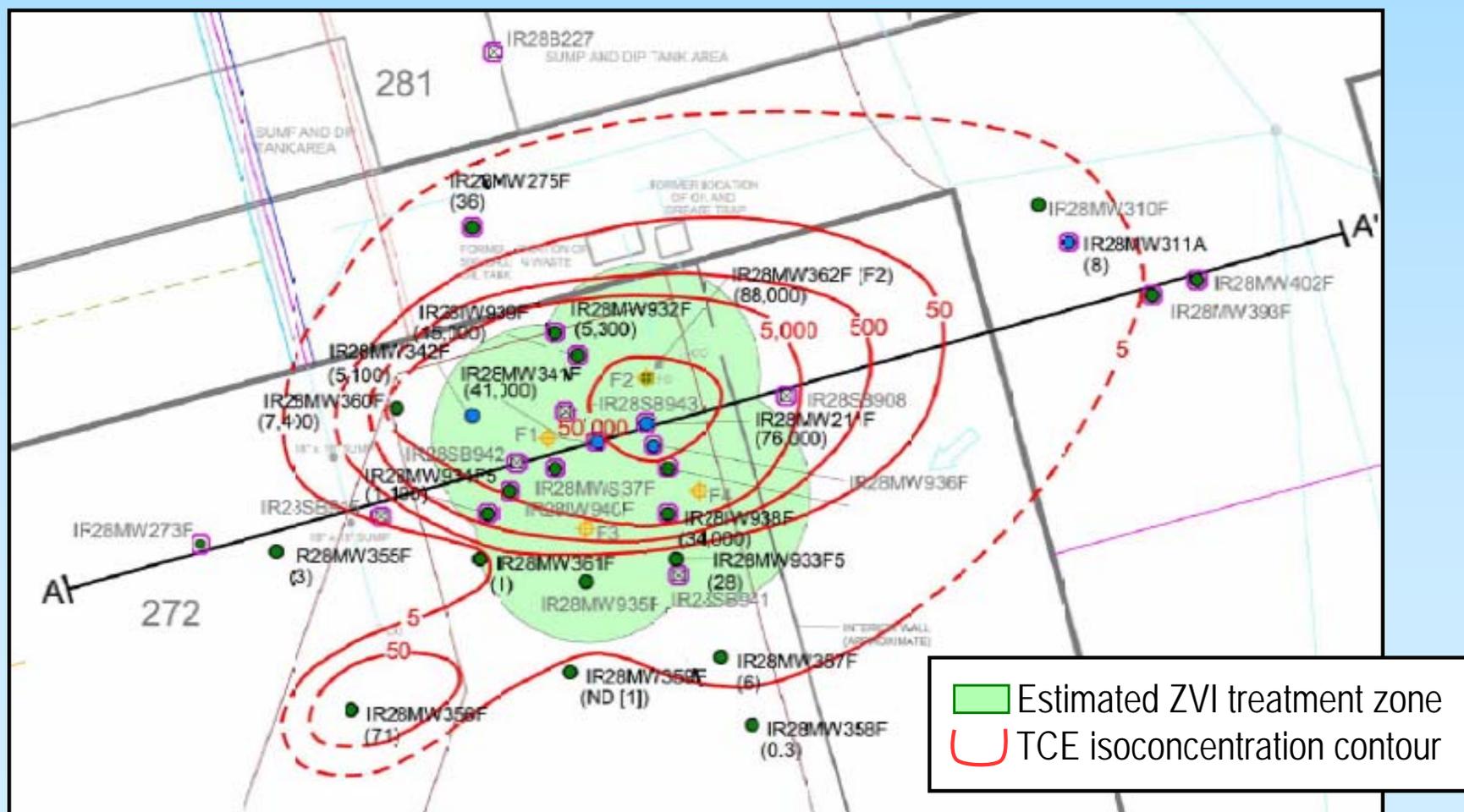
- Hunters Point Shipyard
 - 1869 to 1986 operated as ship repair, maintenance, and commercial facility
 - 1991, designated for closure, divided in Parcels A to F

- Parcel C, Site RU-C4
 - Primary COC, chlorinated solvents, mostly TCE
 - Possible sources include:
 - Former waste-oil UST
 - Grease trap and associated cleanout
 - Five steel dip tanks at a former paint shop

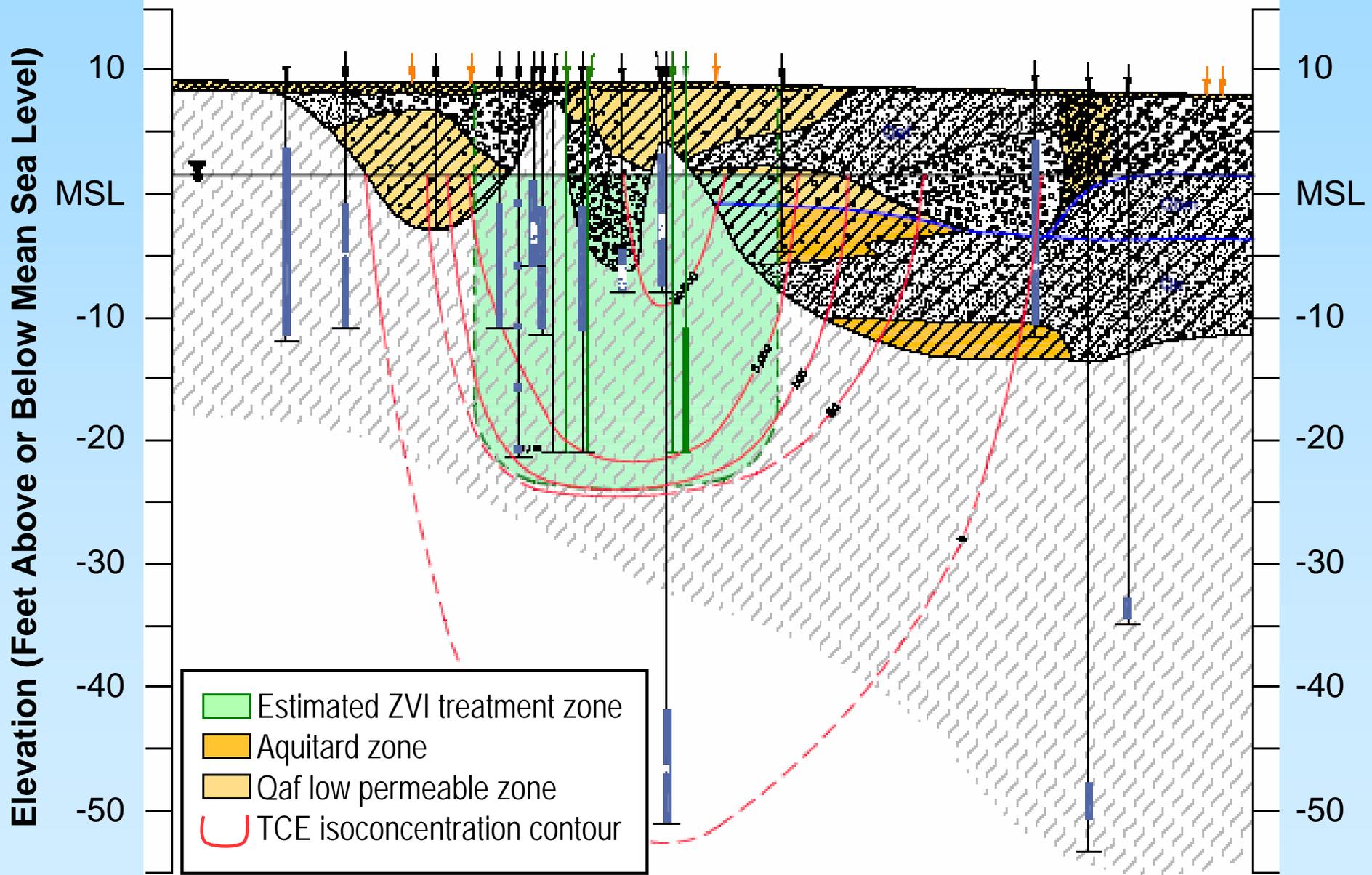
Site Conditions – Contaminant Levels/Extent of Contamination



- Areal extent of treatment area 900 ft²
- Thickness of the subsurface treatment zone 22 ft (730 yd³)



Vertical Distribution of Contaminants/ Site Geology



Technology Implementation (cont.)



30 to 10 ft bgs in 3-ft intervals
Nitrogen gas delivery
55 to 230 psig
1 kg Feroxsm /Gal tap water

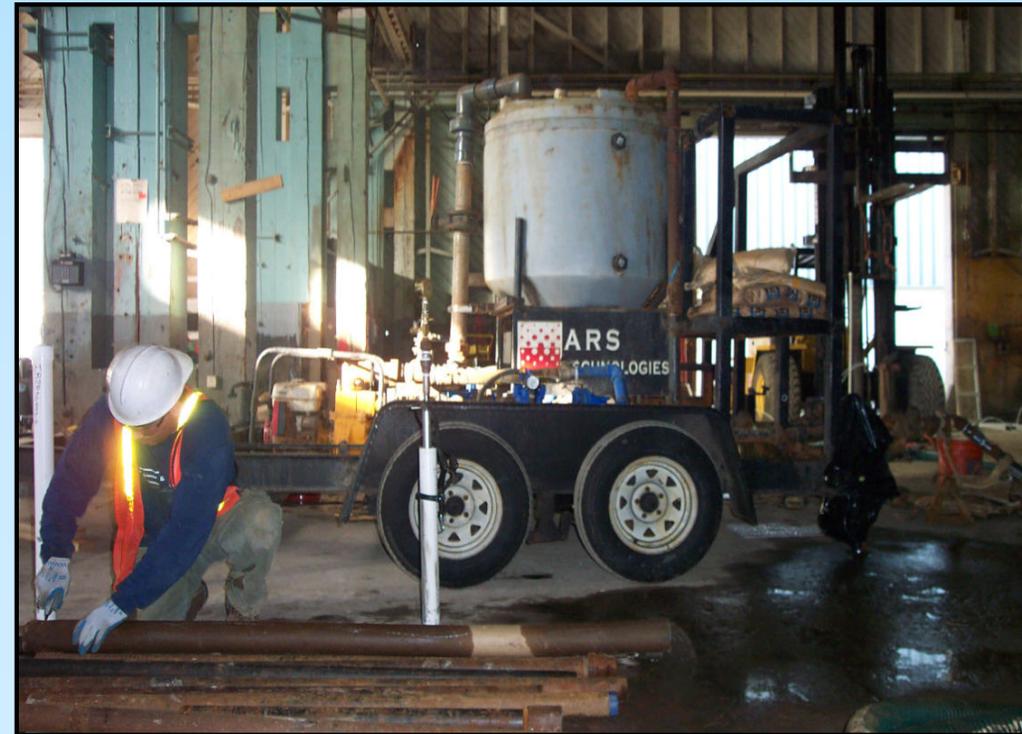


16,000 lb microscale ZVI

Mass Ratios:

Fe/CVOC: ~1,100

Fe/Soil: ~0.008

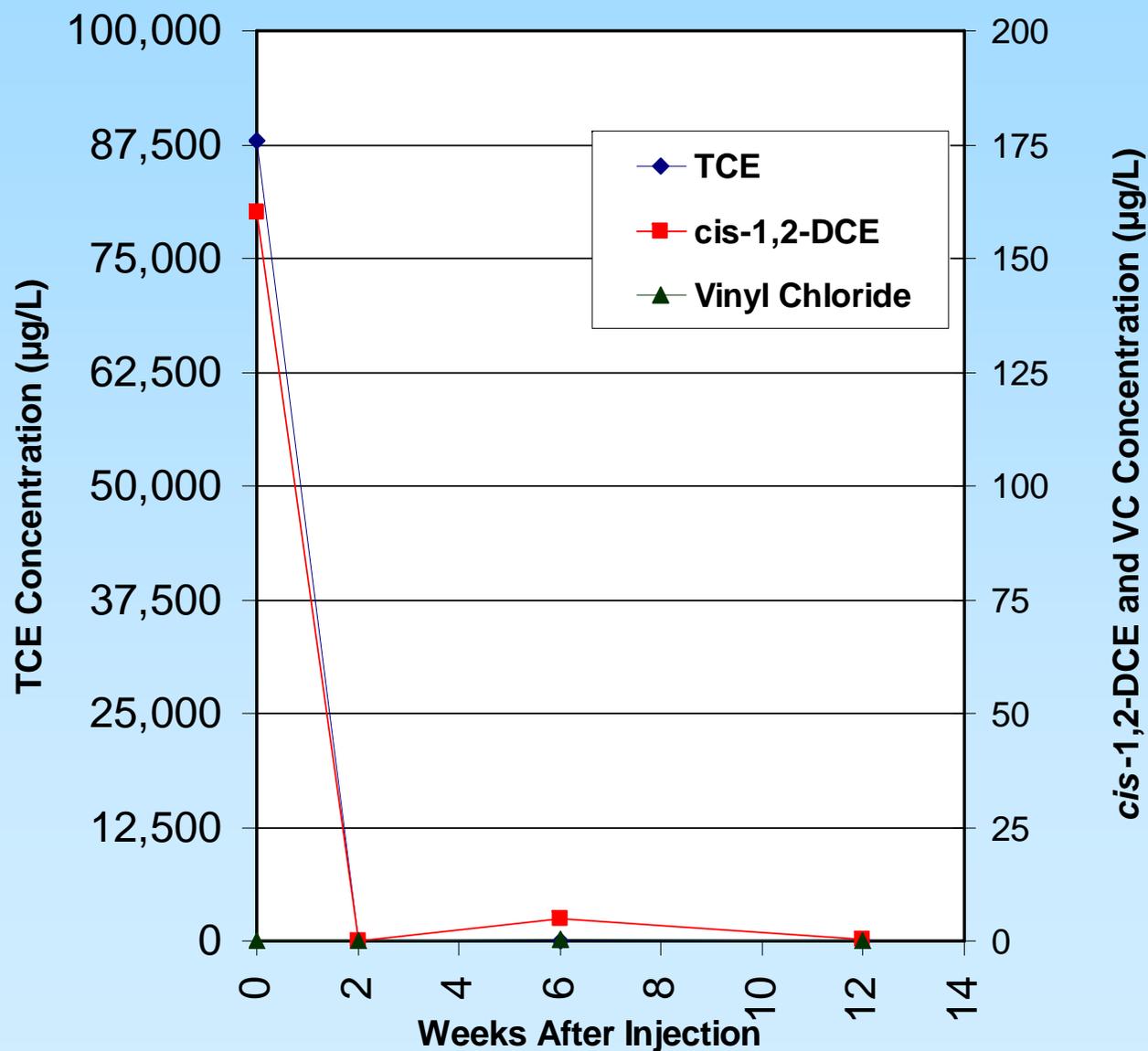


Results – 12-week Performance

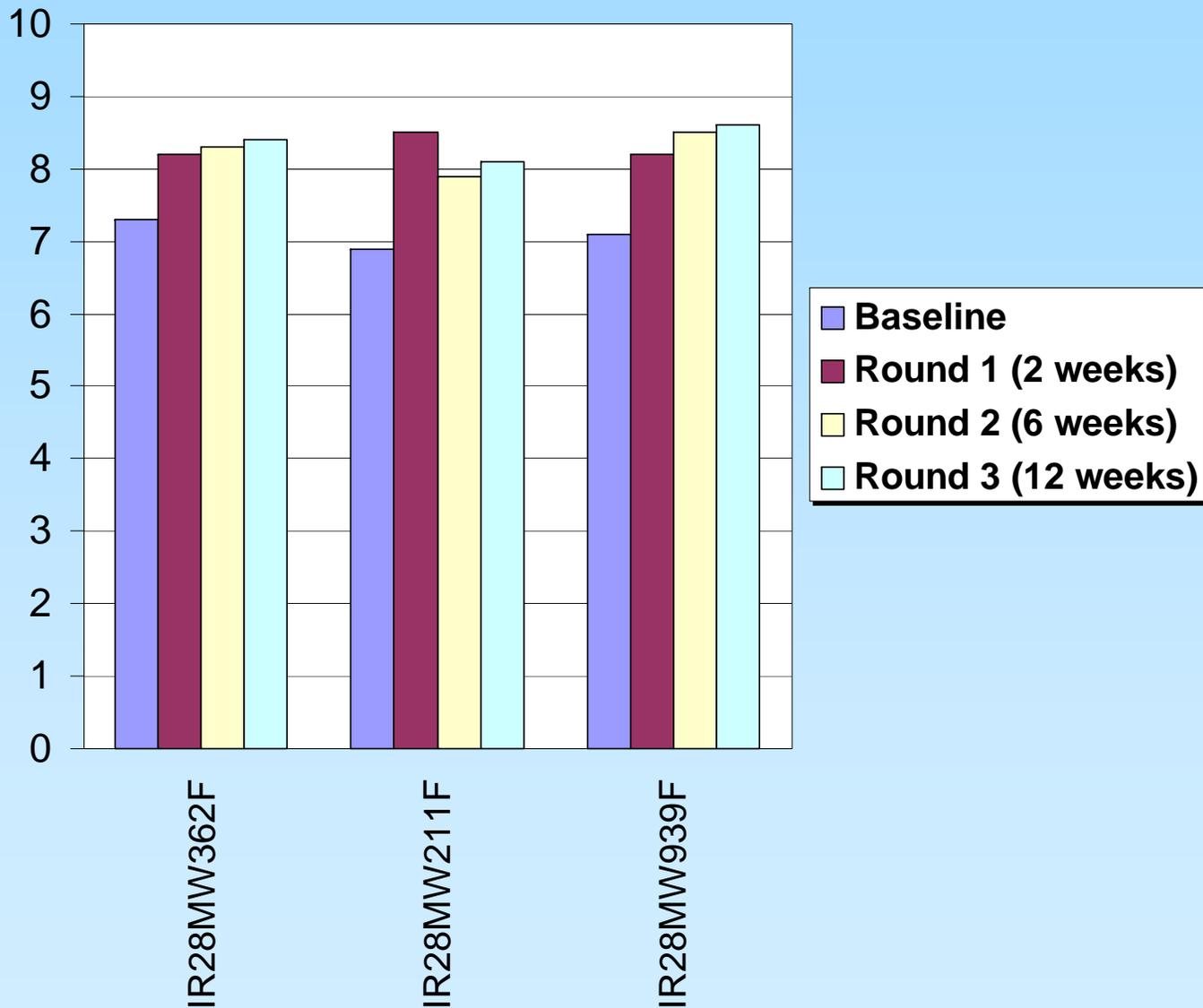


- ~99.2% of TCE in treatment zone reduced to ethane and Cl
 - pre-injection mean 27,000 mg/L
 - post-injection mean 220 mg/L
- Significant decrease in PCE, *cis*-1,2-DCE, VC, chloroform, and carbon tetrachloride (92.6% to 99.4% reduction)
- No significant increase in TCE byproducts (DCE, VC)
- ORP significantly below -200 mV (< -400 mV in some wells)
- pH increased 1 to 2 units

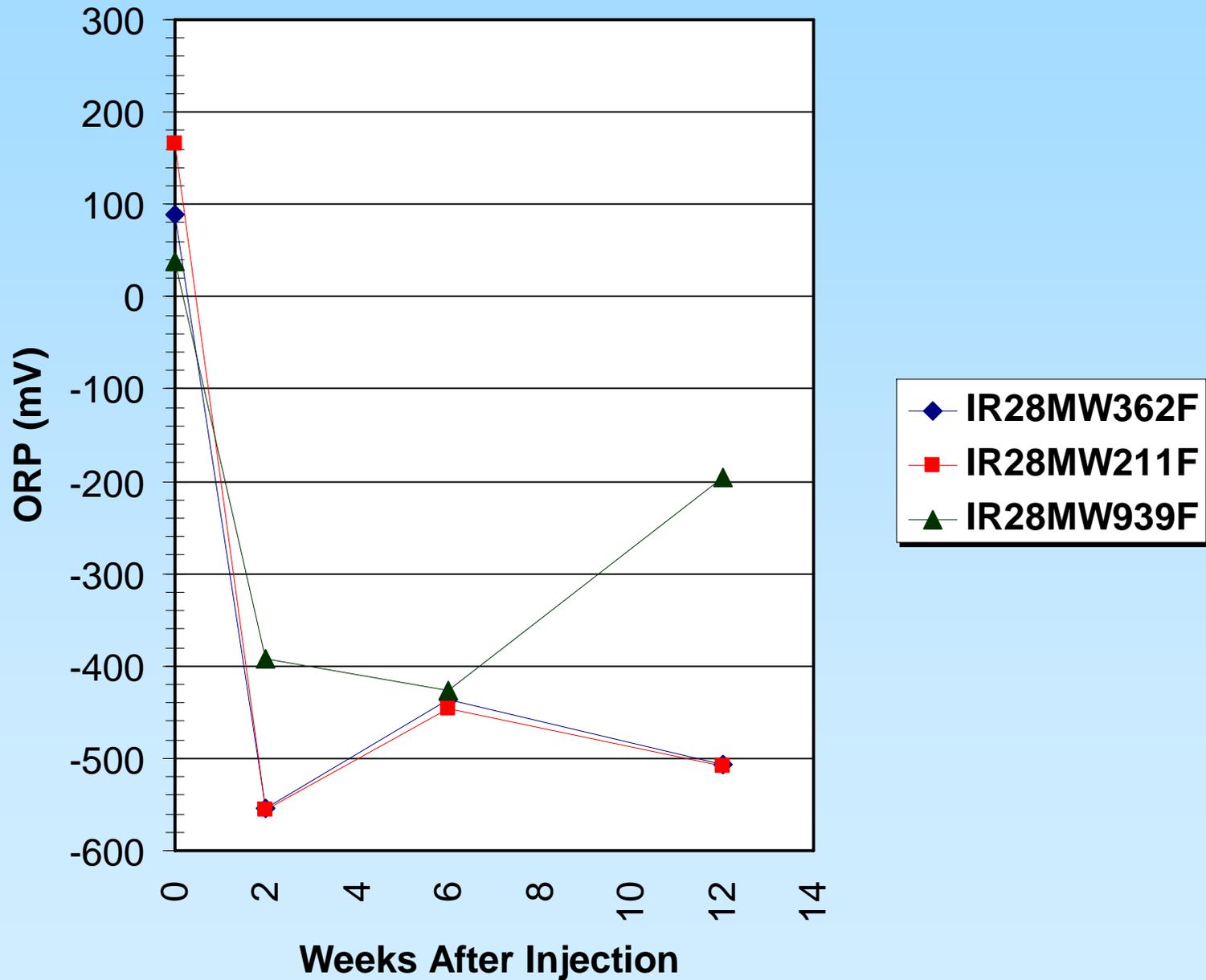
Concentrations in Monitoring Well IR28MW362F



pH after Feroxsm Injection in Source Zone



ORP after Feroxsm Injection



Conclusions/Lessons Learned



- Better to inject iron mass \gg than stoichiometry (1.3 : 1).
- Include long-term performance monitoring measures.
 - Even with excess iron, DNAPL source could be temporarily suppressed, but rebound of dissolved CVOCs could eventually occur.
- ORP is a critical long-term performance parameter.
 - If CVOC levels remain low after ORP rebound occurs, then source treatment is complete.
- Multiple iron injections spaced over a prolonged time period may be required at some sites.

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Case Study 3: NAES Lakehurst, NJ



Areas I and J, Naval Air Engineering Station, Lakehurst

- Principal contaminants: PCE, TCE, TCA, *cis*-DCE, and VC
- Contamination extends 70 ft below groundwater table. Largest mass ~ 45 to 60 ft below groundwater table.
- 300 lb BNP in 18,000 gallons of water injected using submersible pumps and direct push technology
- 5 injection intervals at each location, covering a 20-ft vertical depth

Monitored parameters not indicative that source treatment occurred

- Only slight decrease in ORP in 3 of 13 wells; in some wells ORP increased
- pH levels did not increase as expected
- Significant increase in chloride not observed
- Contaminated groundwater may have been pushed radially outward during injection, as indicated by increased contaminant levels in 50% of the monitoring wells one week after BNP injection
- Large amount of water injection may have caused temporary dilution, contaminant levels rebounded
- BNP may have been passivated in highly oxygenated water
- Mass of iron injected may have been insufficient to create strong reducing conditions necessary for abiotic reduction of CVOCs

Overview



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Cost Analysis - Price of Iron



- Price for NZVI has decreased in the past year due to decrease in cost of raw materials, increased manufacturing capacity, and increasing number of suppliers and vendors.
- Unit prices vary quite a bit from vendor to vendor (NZVI product varies from vendor to vendor):

Iron Product	Supplier	Cost
"Catalyzed" BNP (dry NZVI)	PARS environmental	\$31-\$66/lb, depending on type
"Catalyzed" Zloy	OnMaterials, Inc.	\$23/lb
"Catalyzed" PolyMetallix™	Crane Company	\$72-\$77/lb, depending on quantity
"Catalyzed" RNIP	Toda America	\$26-\$34/lb, depending on quantity
Microscale ZVI	ARS Technologies	\$1-\$1.70/lb
Granular Iron	Peerless Metal Products, Master Builders	\$0.40/lb

Cost of Technology Implementation



- Naval Air Station,
Jacksonville, FL

- Field Demonstration: \$259,000

- Mobilization: \$28,000
- Monitoring Well installation:
\$52,000
- Injection/Circulation events:
\$67,000 (\$37,000 of which for
NZVI)
- Monitoring and investigation-
derived waste (IDW) disposal:
\$110,000

- Project Management, Work Plan,
Bench-scale study: \$153,000

- Hunters Point Shipyard,
San Francisco, CA

- Field Demonstration: \$289,000

- Mobilization: \$31,000
- Equipment/Supplies for injection:
\$100,000 (\$32,500 of which for
ZVI)
- Labor/Drilling for injection:
\$62,000
- Monitoring and IDW disposal:
\$93,000

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Summary of Conclusions



- NZVI is a promising technology for source zone treatment
- NZVI must not become passivated during storage or mixing
 - Improve long-term effectiveness
 - Prevent rebound
- Inject sufficient mass of ZVI to achieve required redox conditions in treatment zone
- Tradeoff between finer particle size and persistence in aquifer
- Short-term performance monitoring can be misleading. Identify and address long-term performance goals.

Additional Information Resources



- ERB Web Site

<http://enviro.nfesc.navy.mil/scripts/WebObjects.exe/erbweb.woa>

- T2 Tool <http://www.ert2.org>

- ITRC <http://www.itrcweb.org>

- Cost and Performance Report, Nanoscale Zero-Valent Iron Technologies for Source Remediation (2005, NFESC)

- Final Report, Evaluating the Longevity and Hydraulic Performance of Permeable Reactive Barriers at Department of Defense Sites (2002, <http://www.estcp.org/projects/cleanup/199907v.cfm>)

- Final Design Guidance for Application of Permeable Reactive Barriers for Groundwater Remediation (2000) <http://www.itrcweb.org/prb2a.pdf>