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

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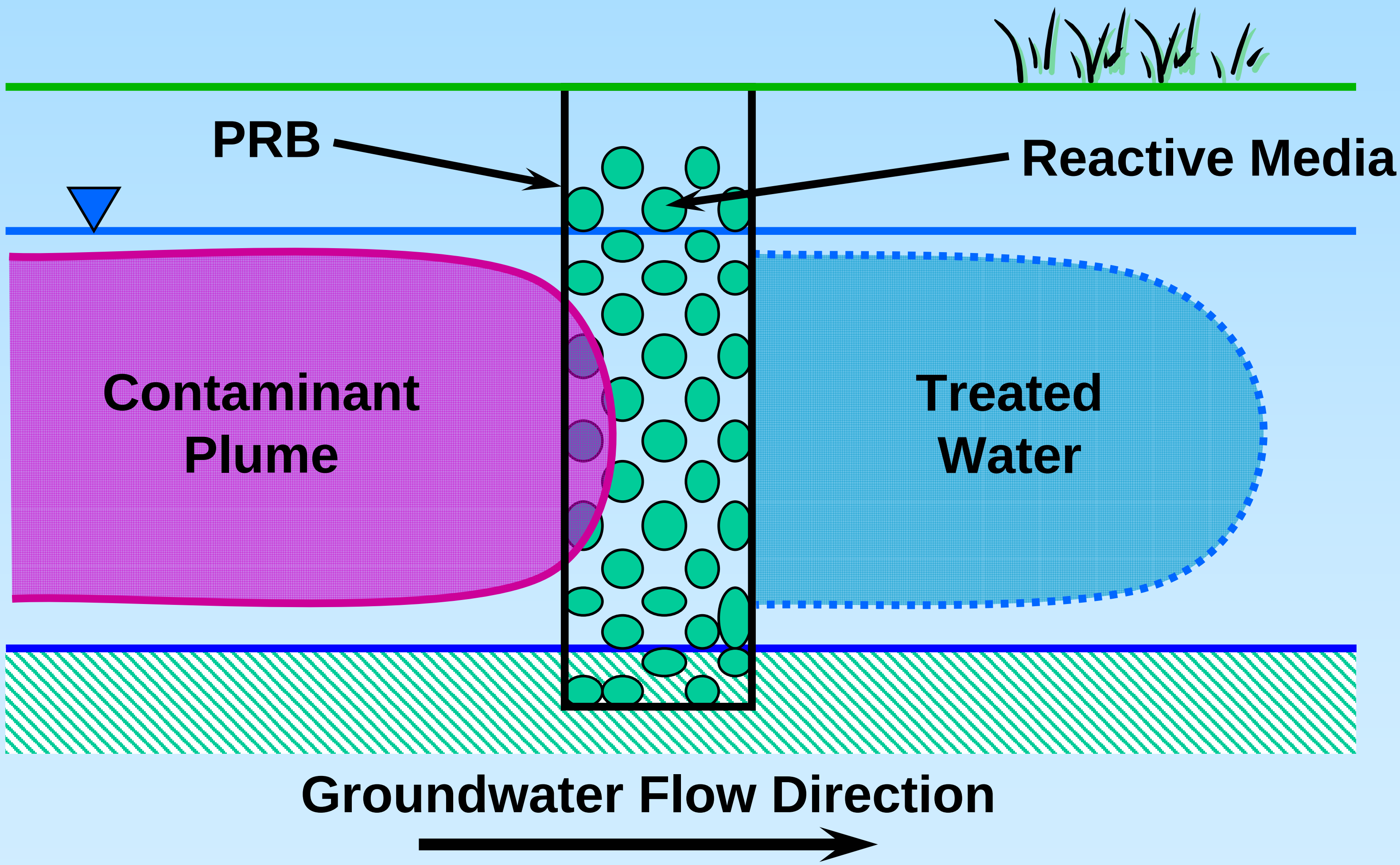
US EPA Workshop on Nanotechnology for Site Remediation
Washington, DC
October 2005

Overview

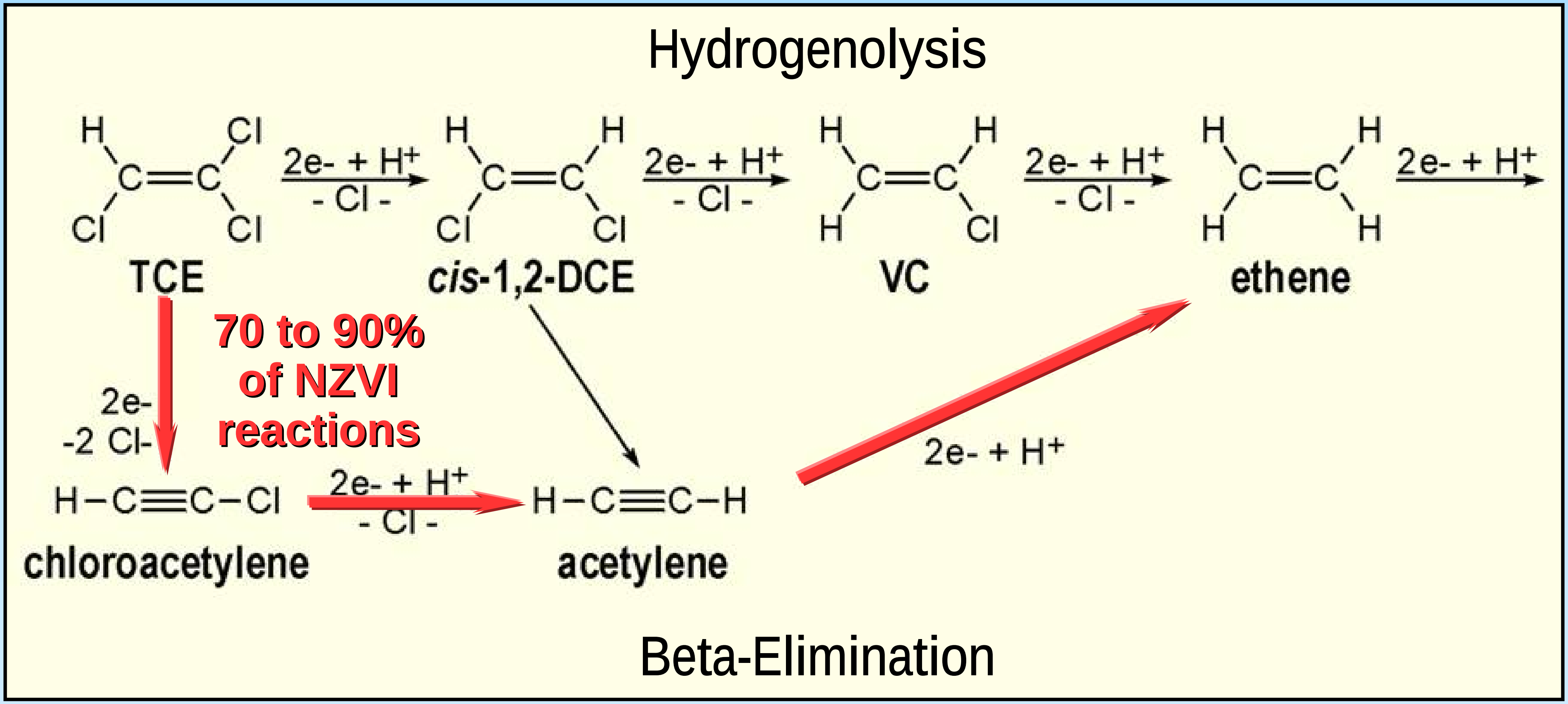
- Introduction
- Case Studies
- Cost Analysis
- Summary of Conclusions

Use of ZVI in Permeable Reactive Barriers (PRBs)

Passive Treatment,
No Aboveground Structures



Multiple Pathways for TCE Degradation



NZVI in Hydraulic Fracture

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- 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

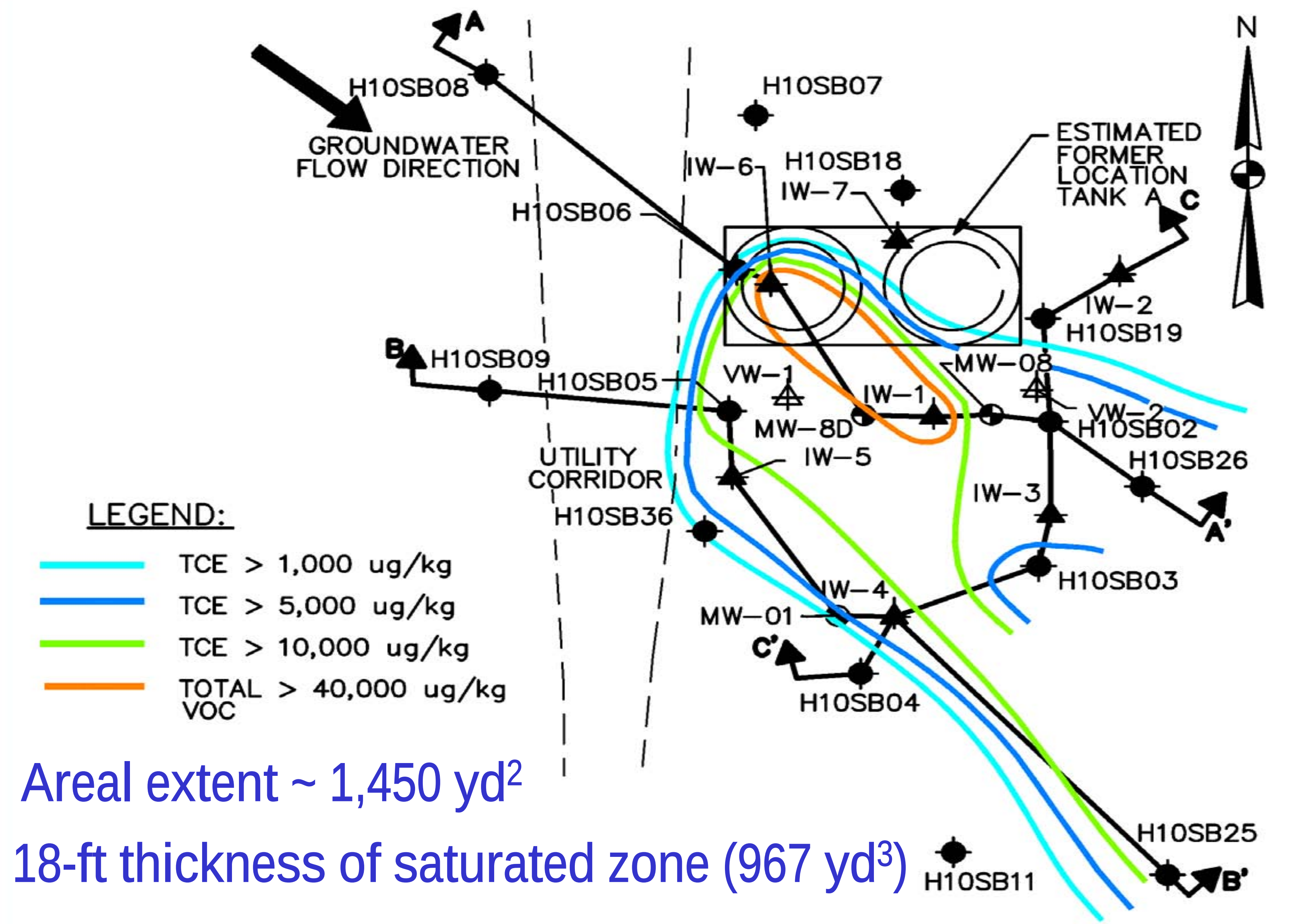
Max soil concentrations:

- PCE – 4,360 µg/kg
- TCE – 60,100 µg/kg
- 1,1,1-TCA – 25,300 µg/kg

Max groundwater concentrations (baseline):

- PCE – 210 µg/L
- TCE – 26,000 µg/L
- 1,1,1-TCA – 8,400 µg/L
- ***cis***-1,2-DCE – 6,700 µg/L

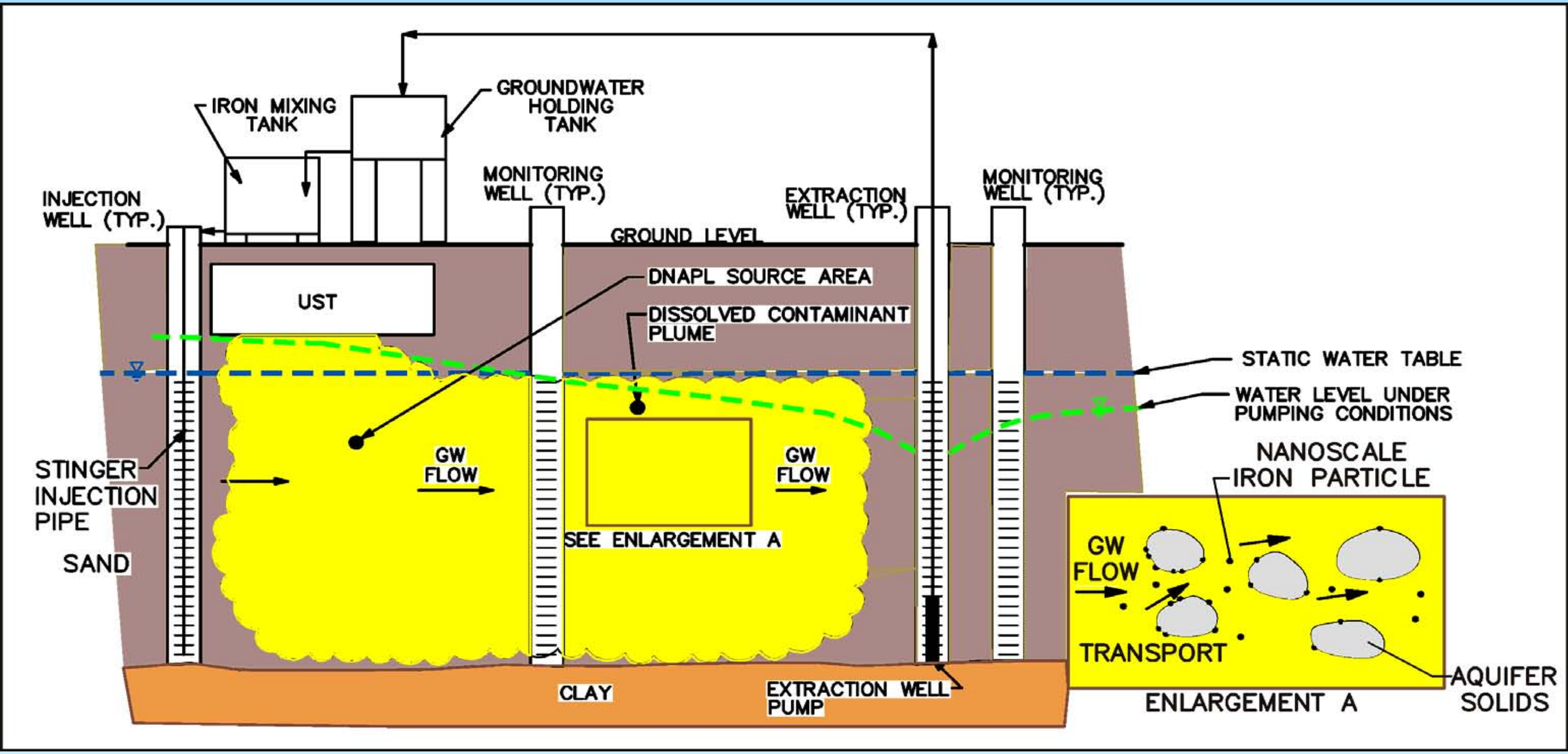
Extent of Contamination



Areal extent ~ 1,450 yd^2

18-ft thickness of saturated zone (967 yd^3)

Technology Implementation



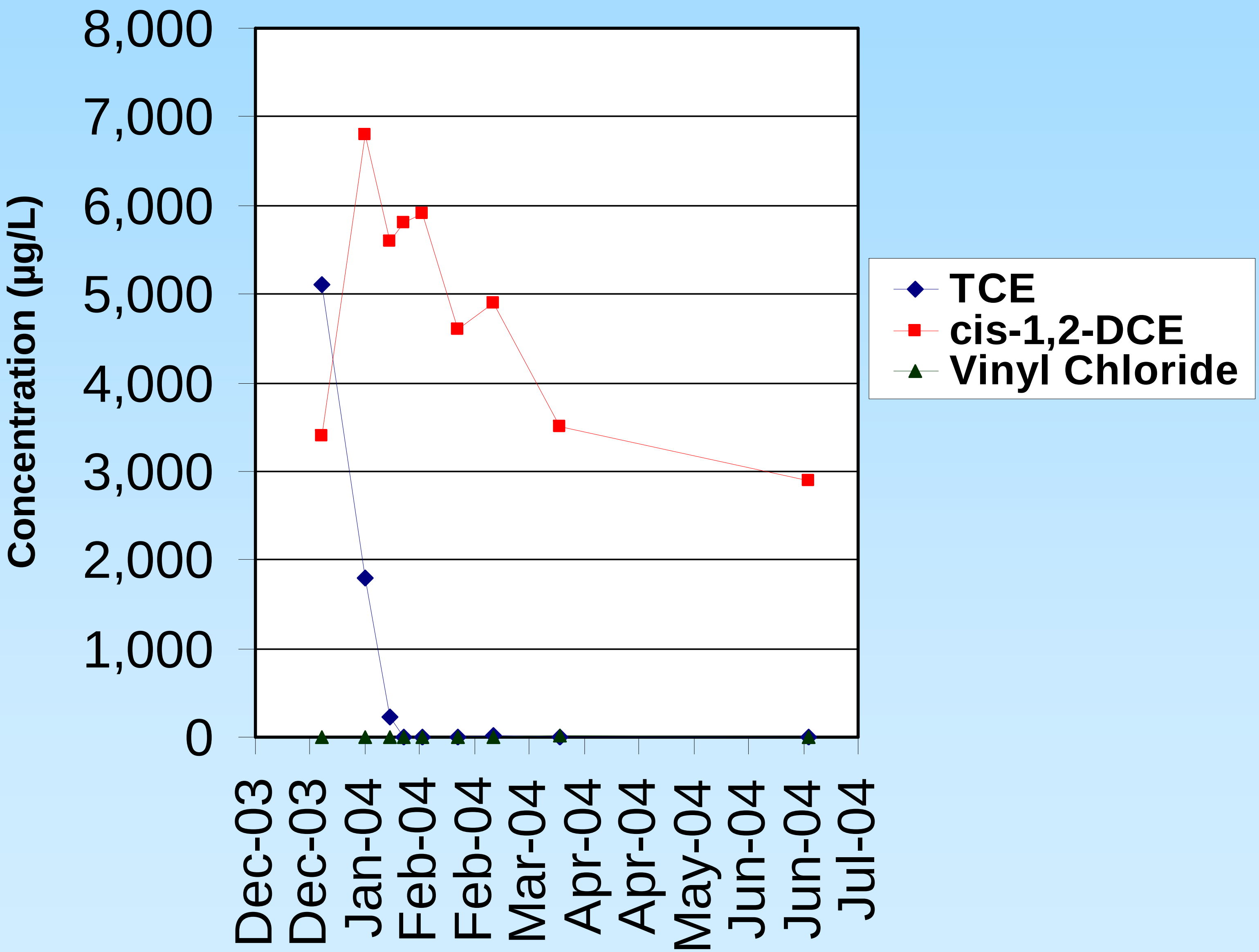
300 lb BNP (99.9 % Fe, 0.1 % Pd and polymer support)

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)

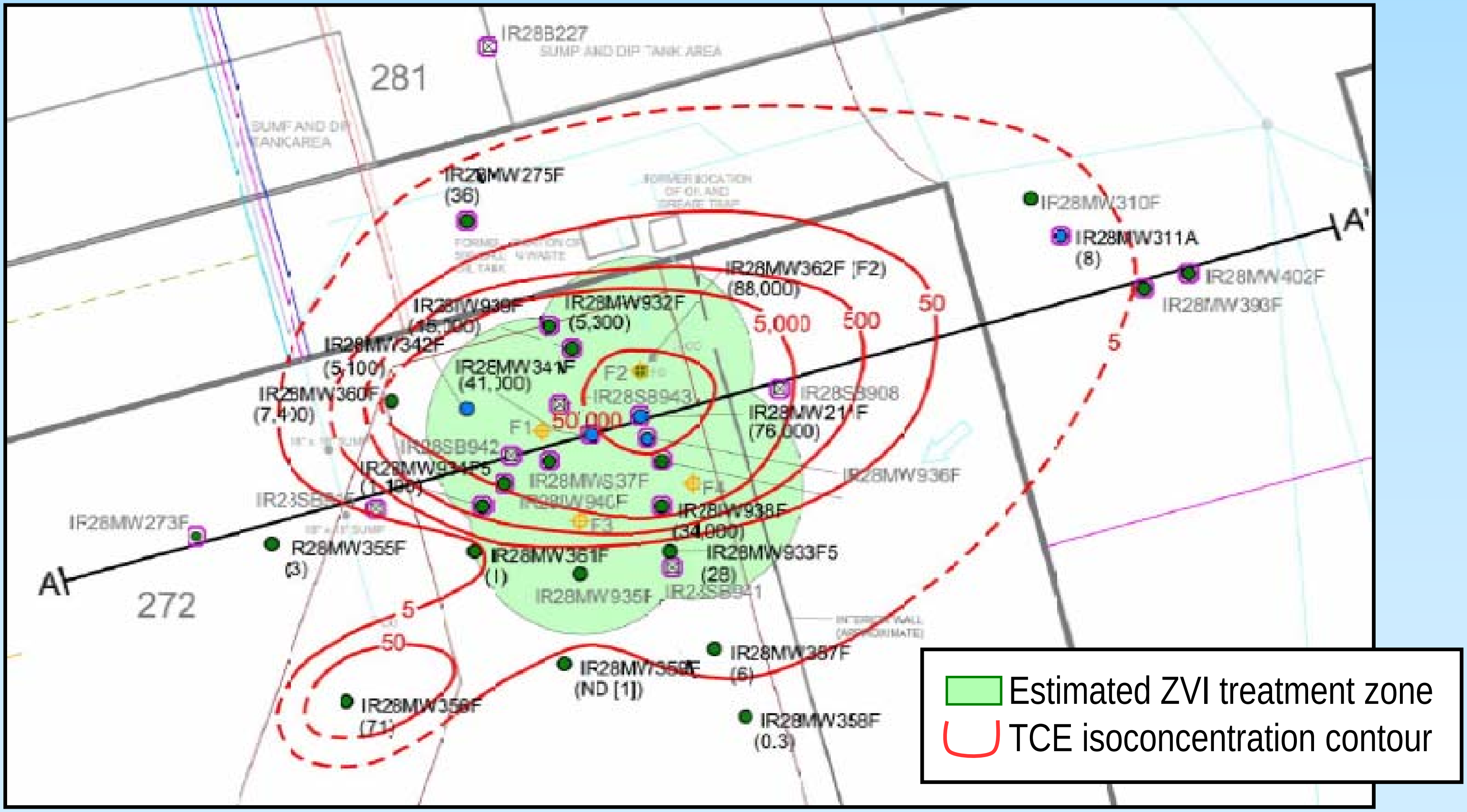
- Site History
- Site Conditions
  - Contaminant Levels/Extent
  - Hydrogeologic Conditions
- Technology Implementation
- Results
- Conclusions/Lessons Learned

Site History

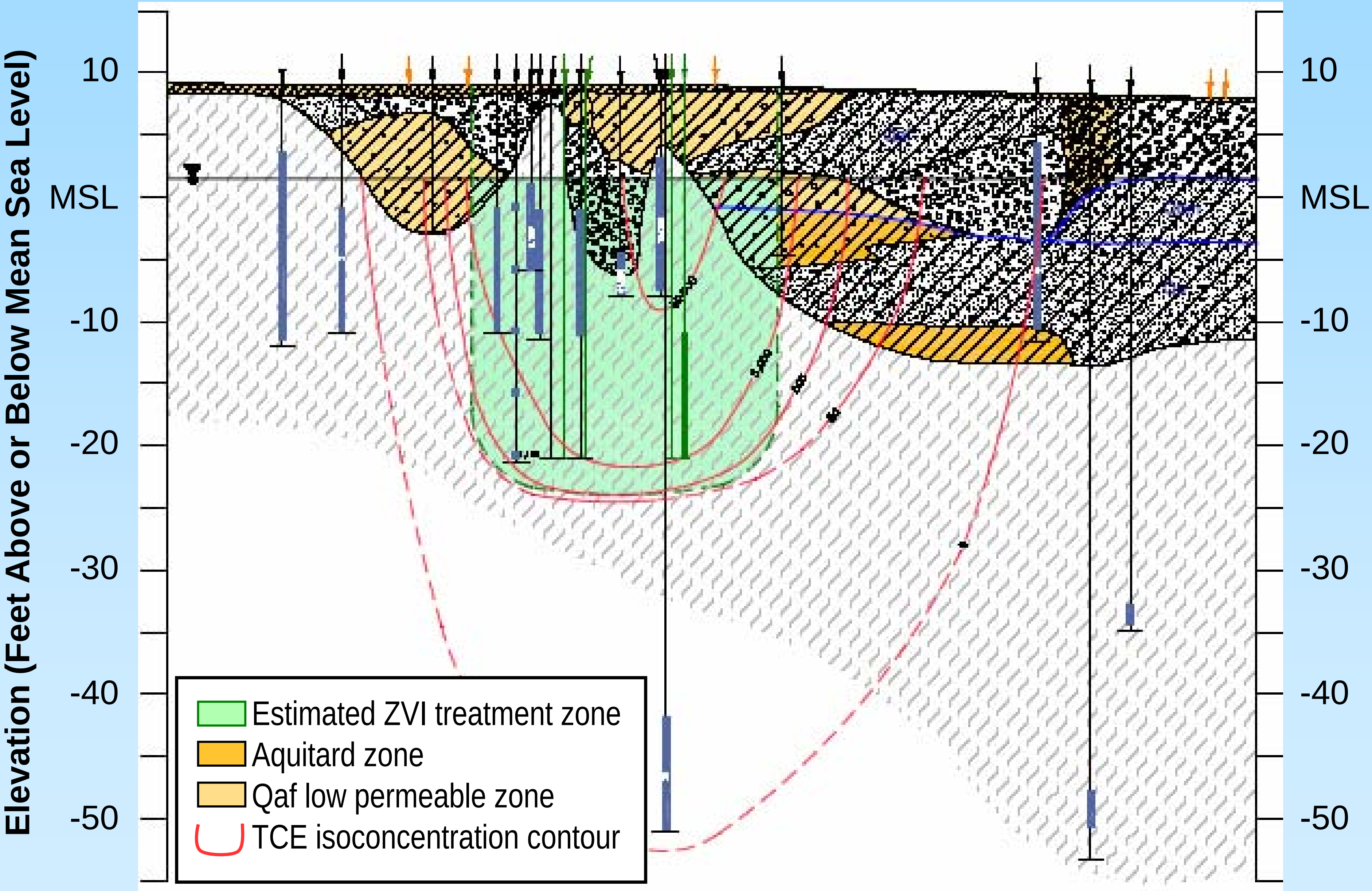
- Hunters Point Shipyard
  - 1869 to 1986 operated as ship repair, maintenance, and commercial facility
  - 1991, designated for closure, divided in Parcels A to F
- Parcel C, Site RU-C4
  - Primary COC, chlorinated solvents, mostly TCE
  - Possible sources include:
    - Former waste-oil UST
    - Grease 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 ft^2
- Thickness of the subsurface treatment zone 22 ft (730 yd^3)



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 Ferox^{sm} /Gal tap water

16,000 lb microscale ZVI

Mass Ratios:

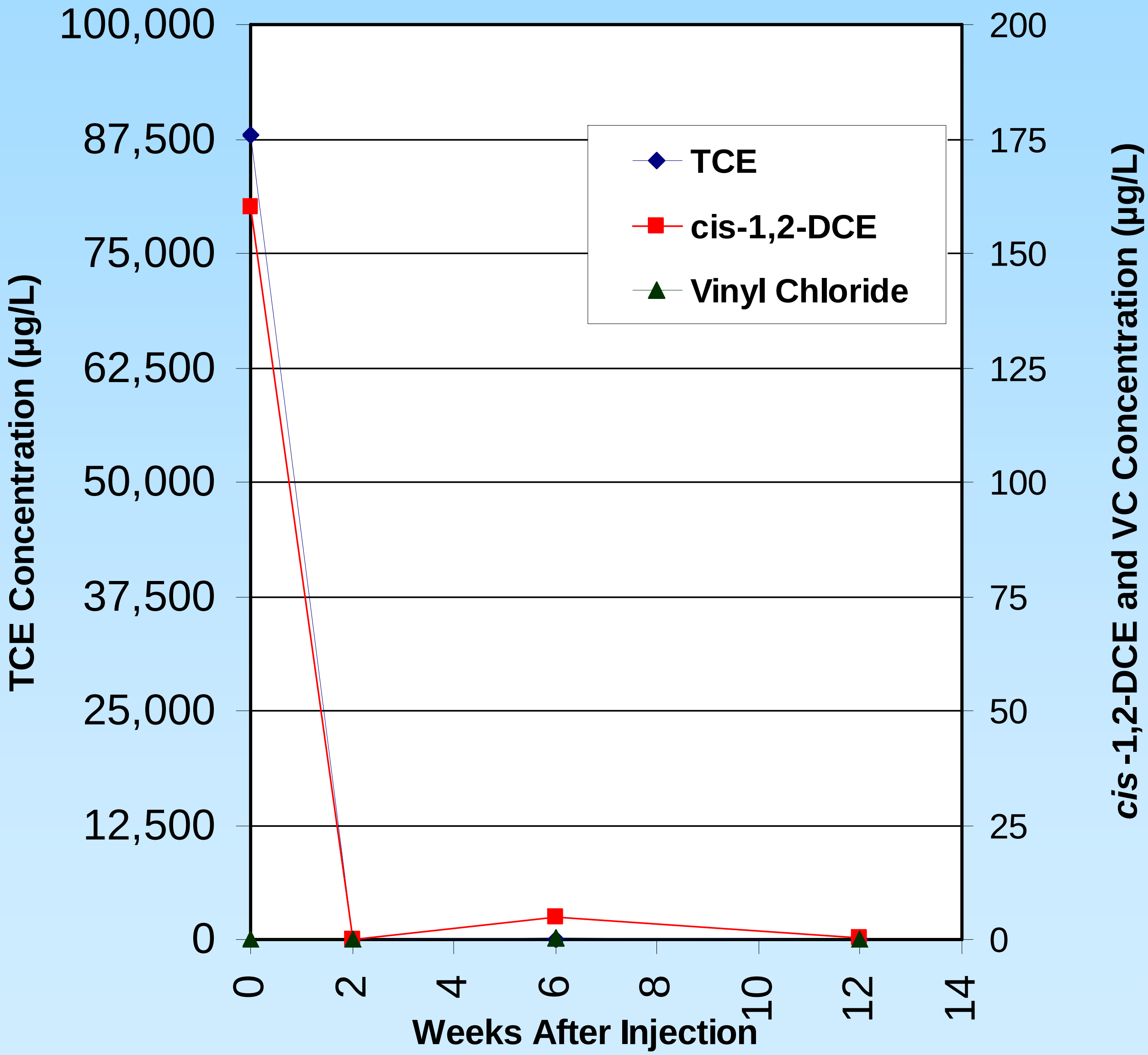
Fe/CVOC: ~1,100

Fe/Soil: ~0.008

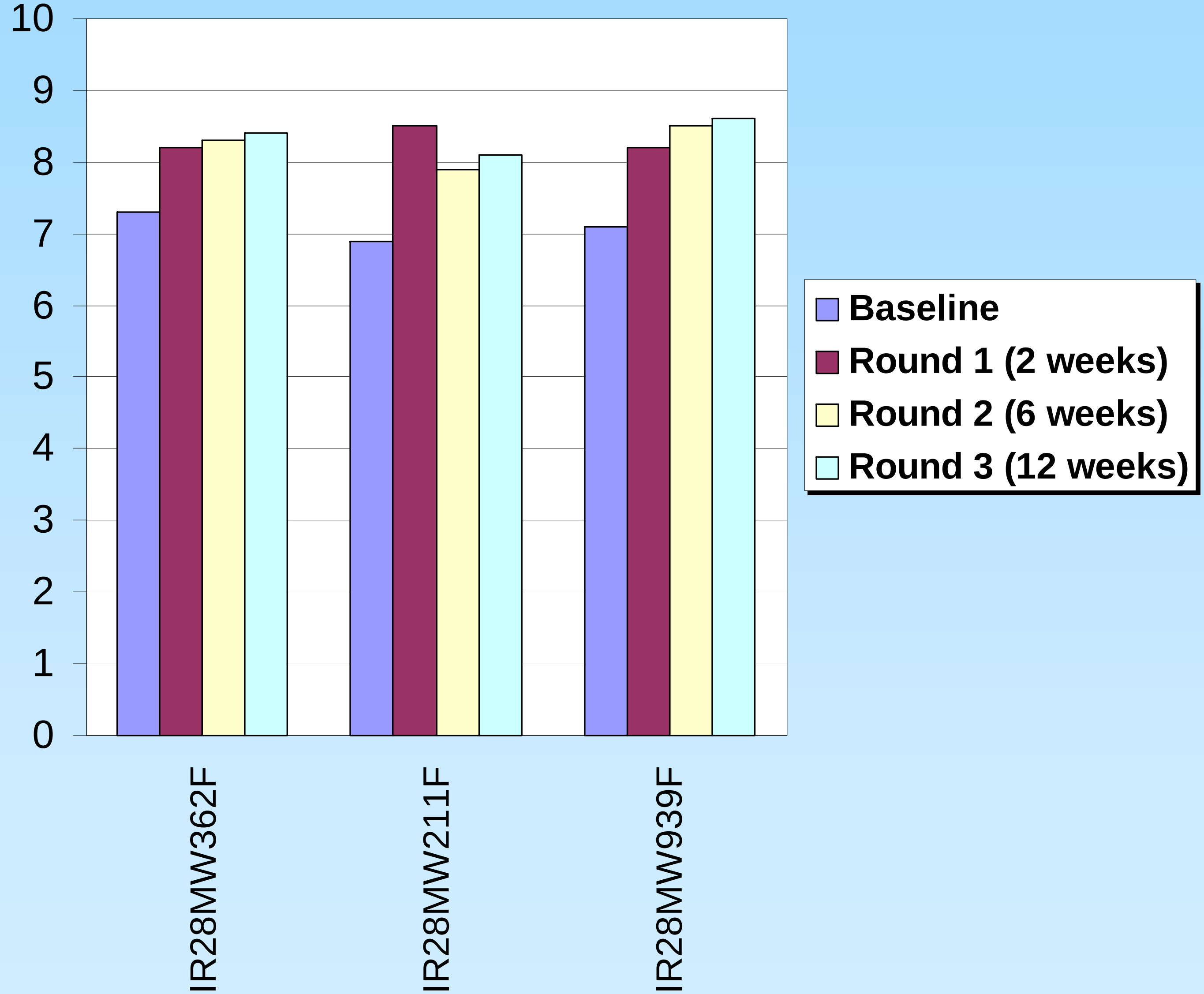
Results – 12-week Performance

- ~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

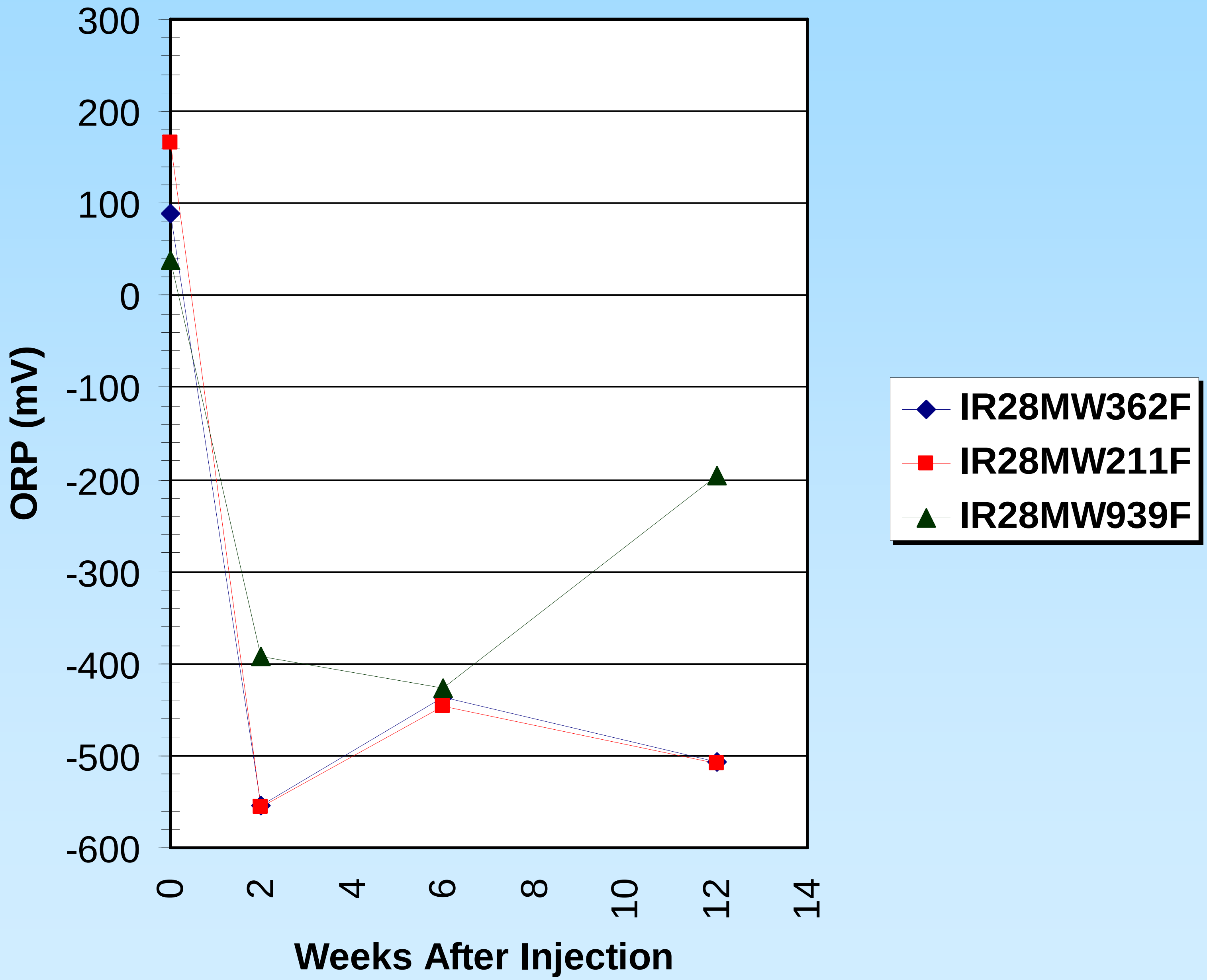
Concentrations in Monitoring Well IR28MW362F



pH after Ferox[sm] Injection in Source Zone



ORP after Ferox^{sm} Injection



Conclusions/Lessons Learned

- Better to inject iron mass >> 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

NAES Lakehurst, NJ Conclusions

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

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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