Nanotechnology Applications for Remediation: Cost-Effective and Rapid Technologies; Removal of Contaminants From Soil, Ground Water; and Aqueous Environments

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Presentation Outline

- EPA – Superfund Program Overview
- Other Federal Programs
- Ongoing Federal Remediation Projects
  - U.S. Navy
  - NASA LC34

The Site Clean-Up Process

Superfund

Preliminary Assessment/Site Inspection (PA/SI)

Scoring (HRS)**/Listing** (NPL)

Remedial Investigation/Feasibility Study (RI/FS)

Record of Decision (ROD)

Remedial Design/Remedial Action (RD/RA)

Operations and Maintenance (O&M)**, includes monitoring**

Closeout/Deletion

General

Site Assessment

↓

Site Investigation

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Clean-up Options

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Clean-up Design/Implementation

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Closeout/Reuse

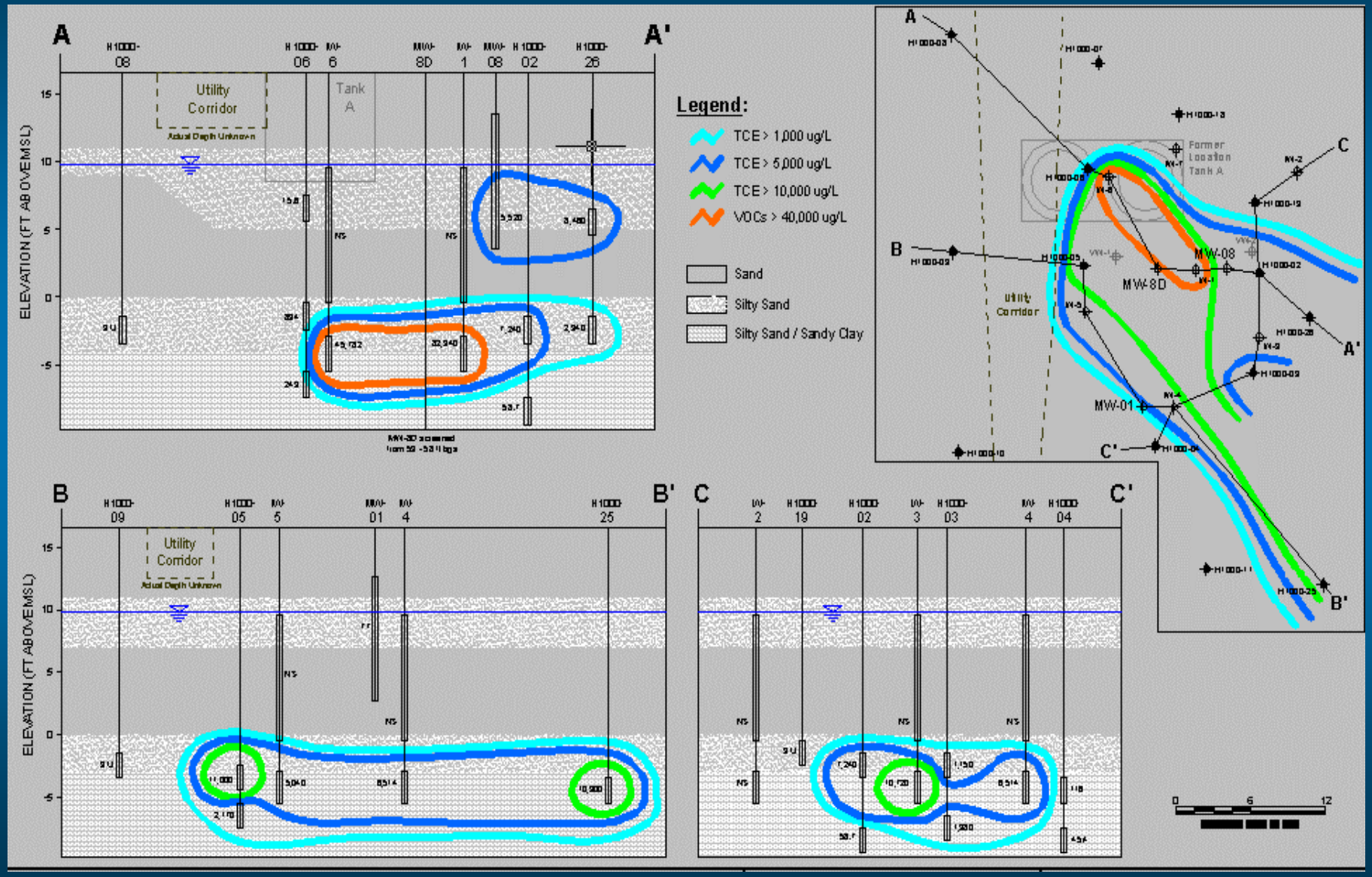
ASTM

Phase I

Phase II

Phase III

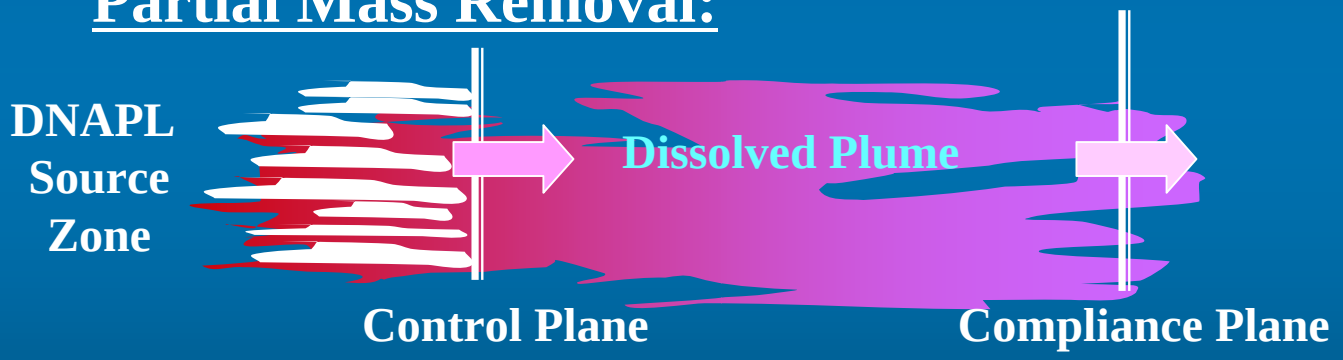
Site Conceptual Model



PLUME RESPONSE

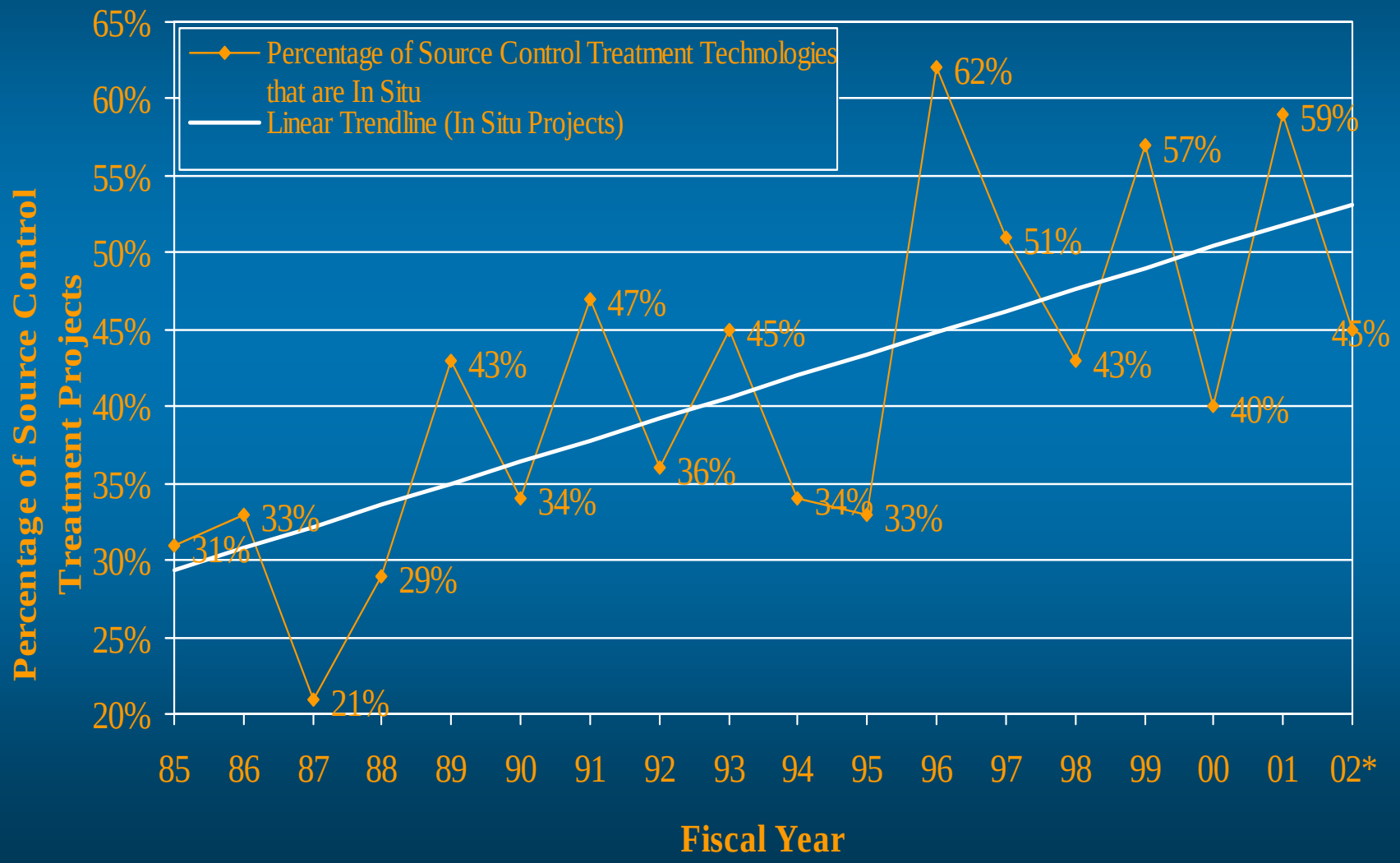
Pre-Remediation:

Partial Mass Removal:



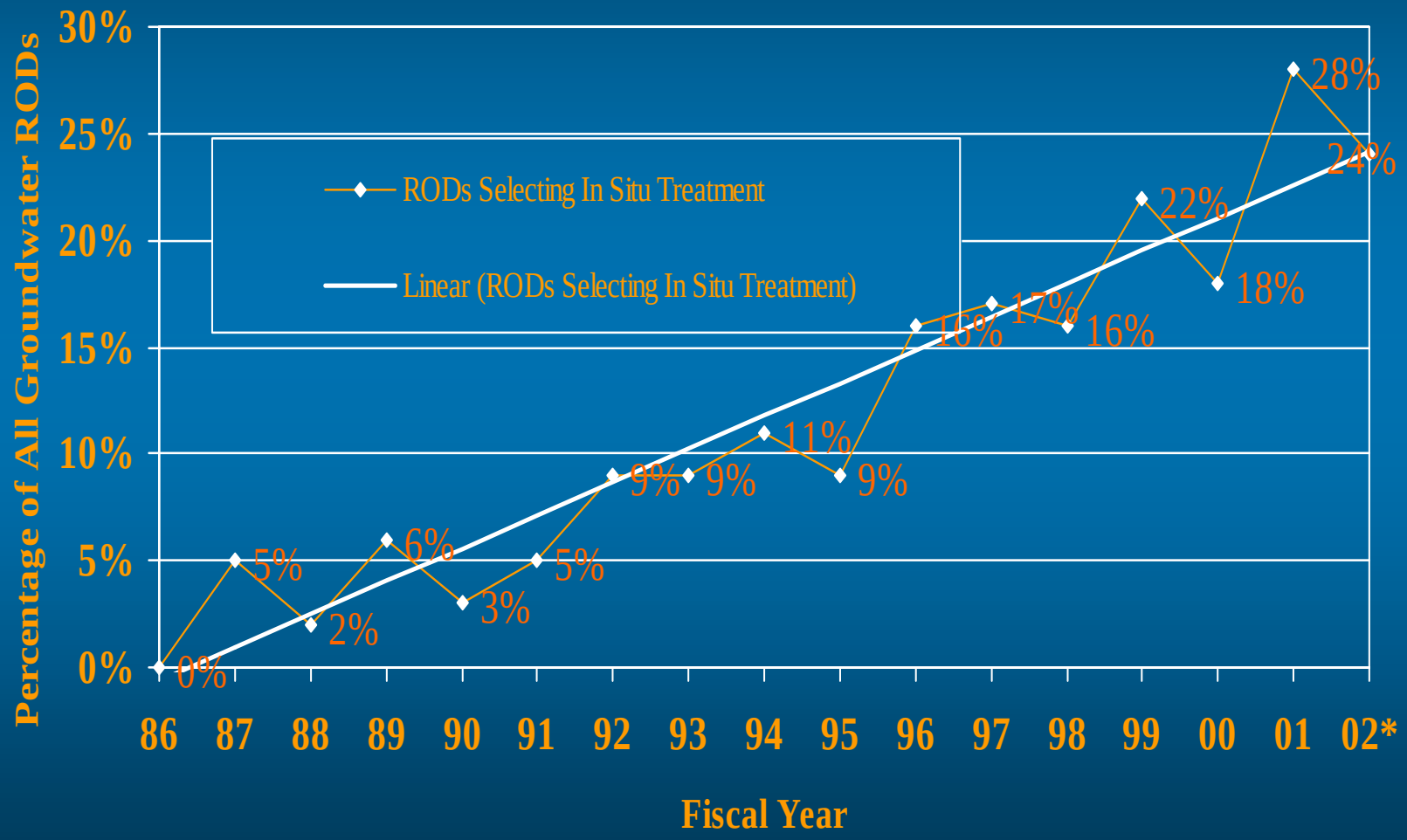
Partial Mass Removal + Enhanced Natural Attenuation:

In Situ Technologies for Source Control*



* Includes information from an estimated 70% of FY 2002 RODs.

Trends in the % of GW RODs Selecting In Situ Treatment (FY86- 02)*



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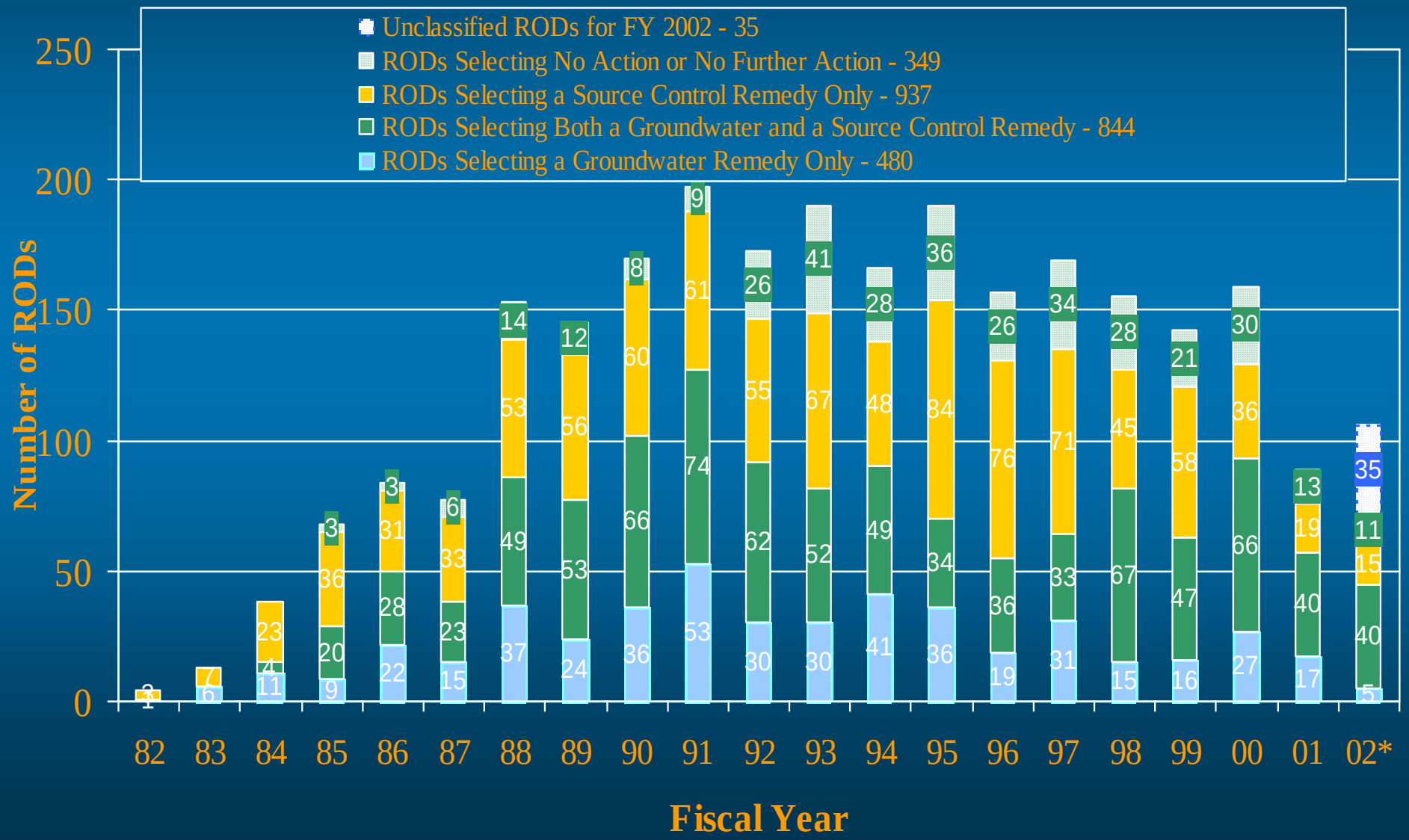
RODs Selected by Year



Program Findings

- Fewer Records of Decision (RODs) are being signed, but these are becoming more complex with a greater mix of remedies (see drop in single media RODs for SC & GW)
- More treatment is taking place for both source control and groundwater, more of that treatment is in situ, and the trend is upward
- Since the beginning of the program, treatment has been selected for either soil or groundwater at 62% of Superfund sites
- There is a clear indication of progress in the program as measured by stage the remedies are in. More have been completed, and more are operational

Sites May Be More Complex

The ASR reports that number of RODs in 2001 and 2002 was about one-third less than the 1988-2000 average. The following help understand why this may be:

- There is a greater proportion of RODs addressing **both** soil and groundwater, an indication of the complexity of contamination at sites on the NPL still requiring RODs.
- There are more combinations of remedies in Groundwater Records of Decision. Previous GW RODs often contained a single remedy (mostly P&T).
- More in-situ treatment is taking place, for both soil and GW. In situ treatment remedies typically address technically complex contamination problems

Future Remediation Market in the U.S.

(From *Cleaning Up the Nation's Waste Sites: Markets and Technology Trends,* EPA-542-*R-96-005)*

Program	# of Sites	Approximate Cost (in billions)
Superfund	550	7
RCRA Corrective Action	3,000	39
USTs	165,000	21
Dept. of Defense	8,300 (at 1,560 installations)	**29**
Dept. of Energy	10,500 (at 137 installations)	**63**
Other Federal	700 installations	**15**
States	29,000	13
		187

Florida DEP's Drycleaning Solvent Cleanup Program

- Success over 2½ years
- 10 contractors
- 156 assessments completed
- 100 cleanups underway
- Information on state drycleaning efforts:
  - State Coalition for Remediation of Drycleaners, http://www.drycleancoalition.org/
- Interstate Technology Regulatory Council (ITRC)
  - http://www.itrcweb.org

Superfund Databases

- Clu-in
  - Web seminars
- Reach it (www.epareachit.org)
  - 2,000 - 4,000 visits/month
  - Most frequent searches by contaminant and media
    - Heavy metals, BTEX, chlorinated VOCs, PCBs
  - Most frequent technologies searched
    - Chem Redox
    - Bioremediation- gw (in situ)
    - Solidification/stabilization
    - Phytoremediation

Federal Partners

- National Institutes of Environmental Health and Science – Superfund Basic Research Program
- NASA
- Department of Energy
- Department of Defense
  - Navy
  - U.S. Army Corps of Engineers
  - Air Force (AFCEE)
  - SERDP

Federal Agency Cost and Performance
Points of Contact

Organization	Point of Contact
Army AEC	Layne Young
USACE	Greg Mellema
Navy	Charles Reeter/Joey Trotsky
Air Force	Erica Becvar
ESTCP	Andrea Leeson
DOE	Skip Chamberlain
EPA	Kelly Madalinski
NASA	Mark Schoppet

Nanoscale Research in DOE Office of Science

- Office of Basic Energy Science (BES)
  - Major source of funding for nanoscale research in DOE SC
  - Supporting construction of 5 Nanoscale Research Centers
- Office of Biological and Environmental Research (BER)
  - Supports bio/environmental research, some of which has nano-components

Nanoscale Science Research Centers

- Supported by Office of Basic Energy Sciences
- Supports the National Nanotechnology Initiative
- Five new Nanoscale Science Research Centers (NSRCs) to support the synthesis, processing, fabrication, and analysis of materials at the nanoscale
- Premier user centers for interdisciplinary research at the nanoscale
- Provide a gateway to existing major BES user facilities for X-ray, neutron, or electron scattering
- NSRCs will contain clean rooms; laboratories for nanofabrication and one-of-a-kind signature instruments

Nanoscale Science Research Centers

(under design or construction)

- Center for Nanophase Materials Sciences (ORNL)

  Integrate nanoscale science research with neutron science, synthesis science, and theory/modeling/simulation to address nano-dimensioned soft materials, complex nanophase materials systems, and the crosscutting areas of interfaces and reduced dimensionality that become scientifically critical on the nanoscale. Utilize ORNL's unique capabilities in neutron scattering.

- Molecular Foundry (LBNL)

  Provide laboratories equipped with state-of-the-art equipment for materials science, physics, chemistry, biology, and molecular biology

- Center for Integrated Nanotechnologies (LANL & SNL)

  Focus on the path from scientific discovery to the integration of nanostructures into the micro- and macro-worlds

- Center for Functional Nanomaterials (LBNL)

  Investigate chemical and physical response of nanomaterials to make functional materials such as sensors, activators, and energy-conversion devices using existing facilities such as the National Synchrotron Light Source and the Laser Electron Accelerator facility

- Center for Nanoscale Materials (ANL)
  - Conduct research in advanced magnetic materials, complex oxides, nanophotonics, and bio-inorganic hybrids. An x-ray nanoprobe beam line at the Advanced Photon Source will be fabricated and run by the Center for use by its users. The facility will use existing facilities such as the Advanced Photon Source, the Intense Pulsed Neutron Source, and the Electron Microscopy Center

Federal Remediation Technologies Roundtable

http://www.frtr.gov

June 9, 2004

U.S. Navy - Naval Facilities Engineering Command

Nanoscale Particle Treatment of Groundwater

- Naval Air Engineering Station - Lakehurst, NJ

Source Area Treatment with Nanoscale Particles

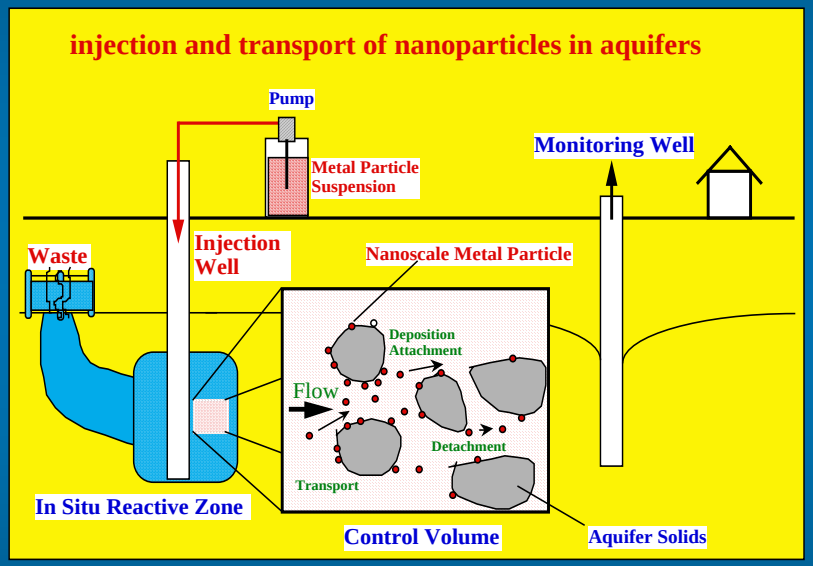
- Naval Air Station - Jacksonville, FL

Micro-Scale ZVI Treatment of Groundwater

- Hunter’s Point Shipyard - San Francisco, CA

NAES Lakehurst

- Used 20 lbs nanoFe/1200 gal water in each of 15 Geoprobe injection points
- Solution injected over a 20-foot interval (50’-70’), in equal 2-ft lifts
- Used GW from nearby extraction well
- A total of 300 lbs NanoFe injected
- TCE levels reduced up to 50% in single injection – additional injection anticipated
- NanoFe = nanoscale iron with a Pd^0 coating (catalyst)
- 1.7 lbs Palladium used in Phase I; 3.75 lbs used in Phase II



NAS Jacksonville

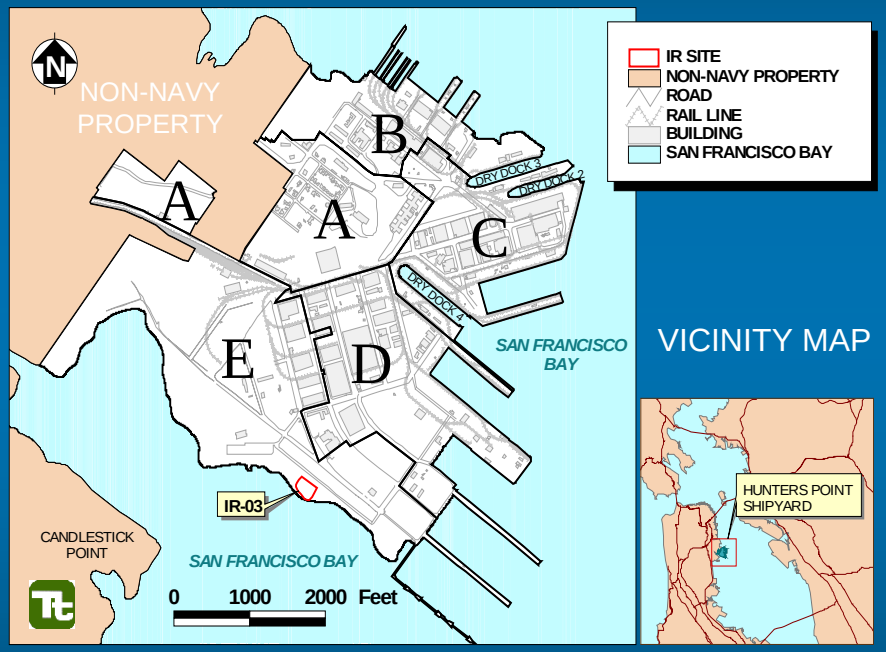
- Nanoscale Iron
  - Food grade Polymer Supported w/Palladium Catalyst
  - Purchased from PARS Environmental
  - CVOC mass estimated: 40 to 125 lbs
  - 300 lbs of iron was injected
  - Costs for the nanoscale iron has dropped 2 times

NAS Jacksonville

- Two injection methods:
  - Strategic DPT injections
  - Recirculation Process
- More work is yet to be done:
  - Groundwater sampling for 3 remaining quarters
  - Confirmation soil sampling
- Cost estimates
  - Current is \$300-350/yd^3
  - Excavation estimated to be \$400-500/yd^3
  - Estimate with less sampling and lower iron costs is \$215-265/yd^3

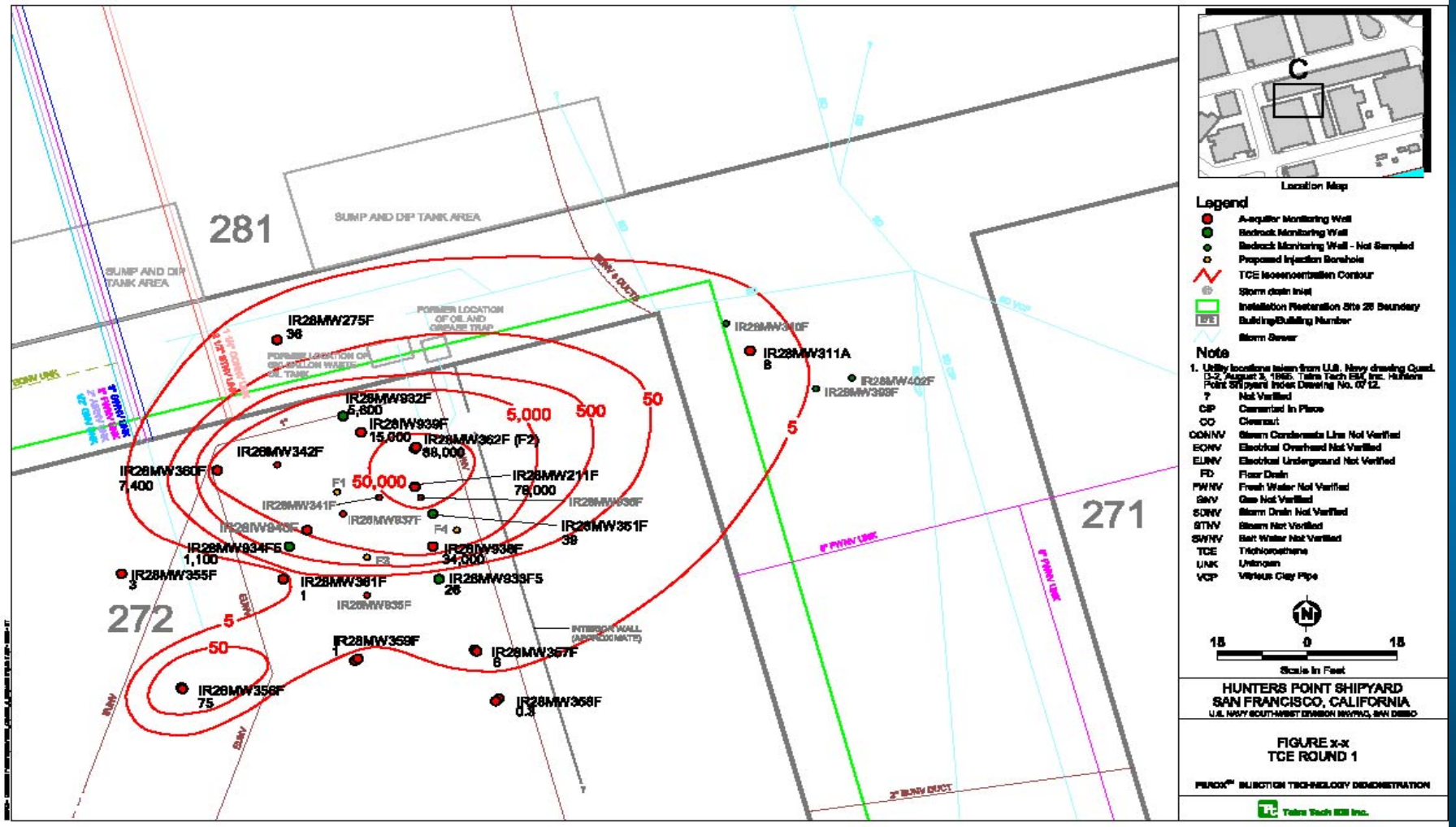
Hunter's Point Location and Site Conditions

- Remedial Unit C4
- Pnuematic fracturing to inject micro-scale ZVI
- Soil type = 10ft layer of artificial fill over fractured bedrock
- Targeted depth is 7ft bgs to 32 ft bgs
- Water table is 7 ft bgs
- TCE present in GW up to 88 mg/l
- Removed 99.1% of total chlorinated solvents

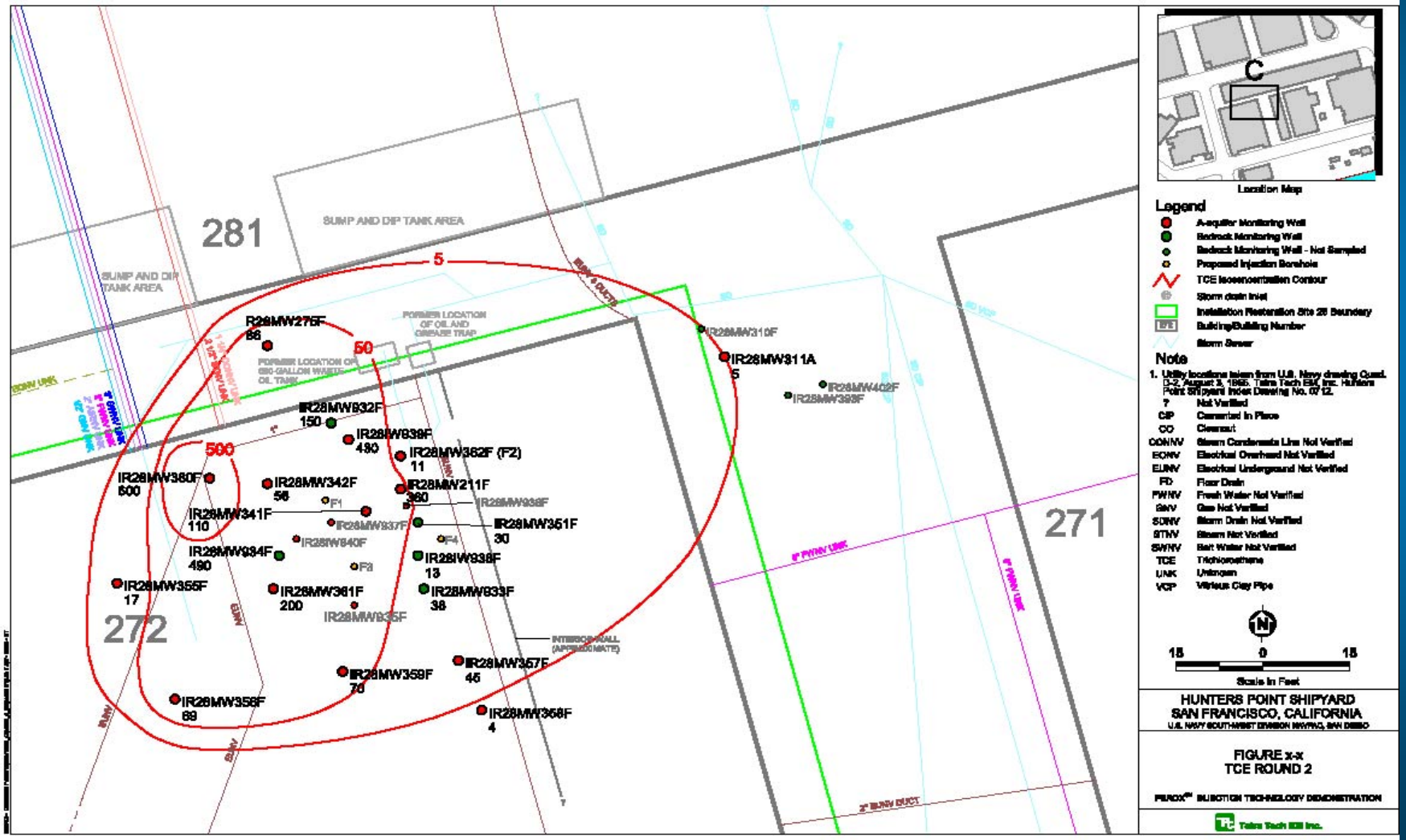


Hunter's Point Shipyard

Hunter's Point - Pre-ZVI Injection



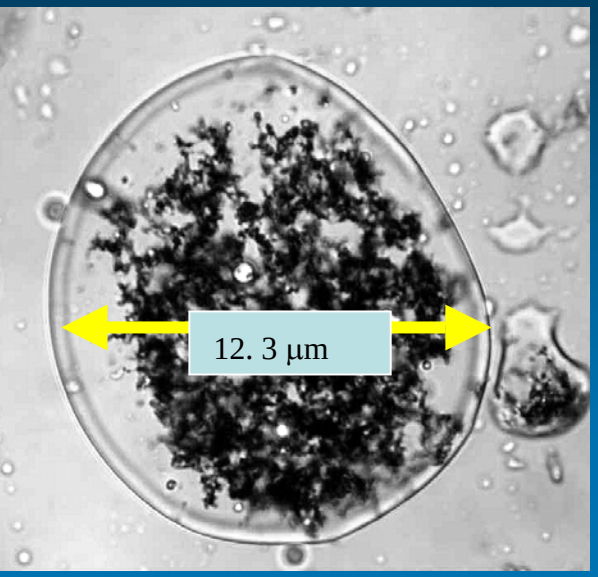
Hunter’s Point - Post-ZVI Injection

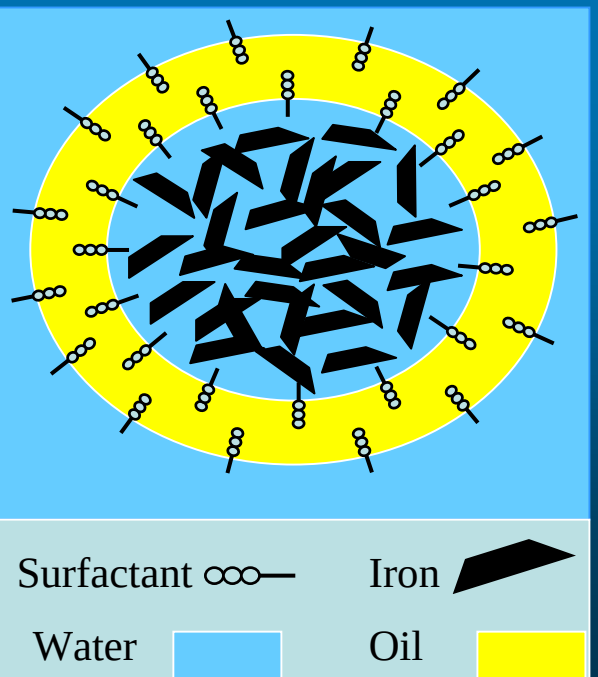


Hunter's Point - Results

- TCE in groundwater was reduced 99.2% in 3 weeks
- Project cost estimate was $117/yd^3
- Plume displacement not significant
- ROI ranges from about 15 to 20 feet
- Applied to additional sites
- Evaluating applicability to other sites

Properties of EZVI

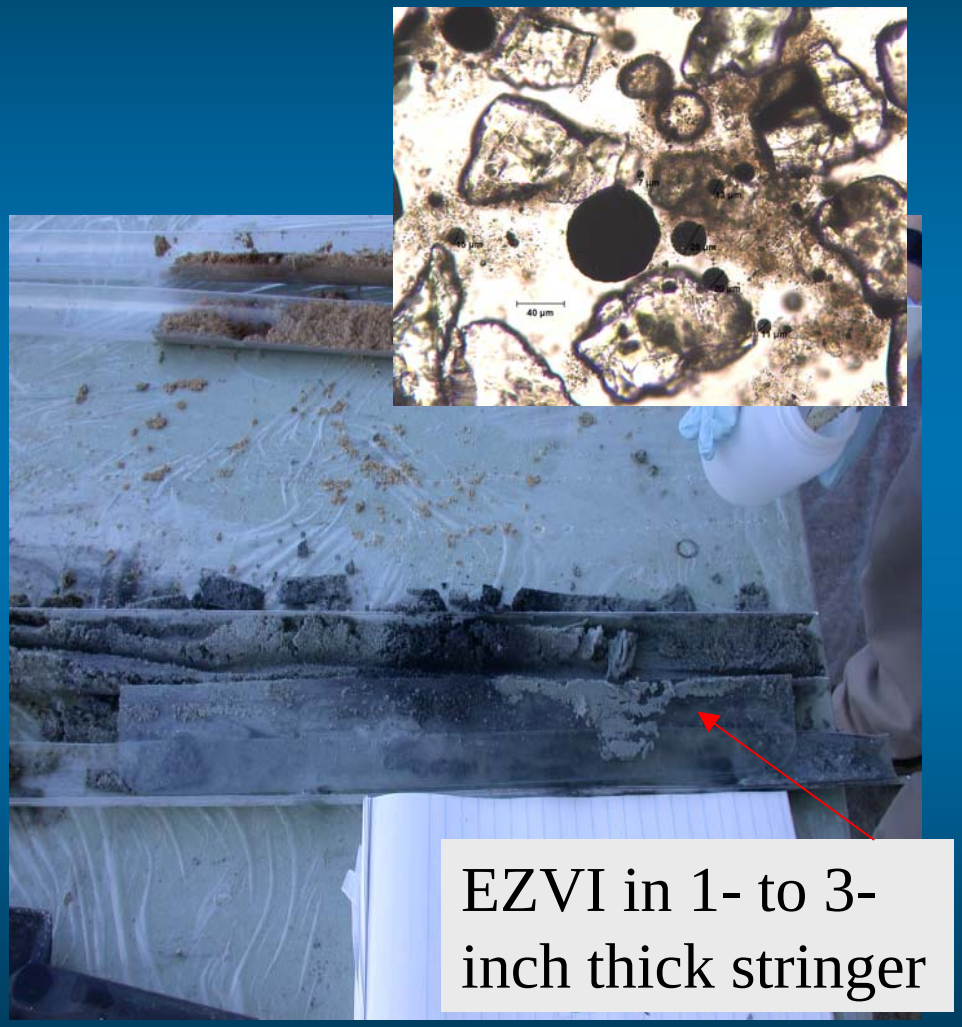




- Since exterior oil membrane of emulsion droplets have hydrophobic properties similar to DNAPL, the emulsion is miscible with the DNAPL.
- CVOCs in DNAPL diffuse through the oil membrane and undergo reductive dechlorination in the presence of the ZVI in the interior aqueous phase.
- In addition to abiotic degradation due to ZVI, EZVI contains vegetable oil and surfactant which will act as long-term electron donors and promotes anaerobic biodegradation.

NASA - Results of Demo at LC34

- Soil Core Samples:
  - Stated objective of 50% removal of total TCE
  - Significant reduction of TCE (>80%) where EZVI was present
  - Average reduction of 58%
  - EZVI migrates to shallow intervals



NASA - Results of Demo at LC34

- Groundwater Samples:
  - Significant reduction (60 to 100%) of TCE in target depths.
  - Reduction of 56% in the Mass Flux.
    - from 19.2 mmoles/ft^2/day down to 8.5 mmoles/ft^2/day
  - 18 months after injection groundwater concentrations indicate that long term degradation due to bioremediation ongoing

Results at LC34

- Elevated cis-1,2-DCE, VC suggest biodegradation due to oil as an electron donor may also be significant
- Bioaugmentation may enhance complete degradation associated with biological component of process

Injection Techniques Field-tested at LC34-2004

- Pressure Pulsing
  - Pneumatic injection of EZVI in sandy soils looks promising. Able to disperse EZVI evenly and at target depths.
  - Further testing using pneumatic injection concludes that micro-scale iron may be injected into sandy formations without emulsion deformation and a sufficient ROI is achievable. Saves $$$$
- Pneumatic Fracturing
- Hydraulic Fracturing
  - Hydraulic fracturing of EZVI does not deform emulsion droplets. May have application in consolidated sediments or where tighter lithologies prevail
- Direct Injection
  - Direct push has application to small sites where a direct push rig can install a bunch of “columns” of EZVI in a single day, making it very cost competitive over injection technologies that seek larger ROIs.