Emulsified Zero-Valent Iron (EZVI) Treatment of Chlorinated Solvents

NAVFAC

Geosyntec Consultants

Past RITS Presentations on ZVI and Bioremediation

- Permeable Reactive Walls (Spring 1998)
- Advances if Permeable Barrier Technologies (Spring 2002)
- In Situ Treatment of Chlorinated Solvents Using ZVI Technologies (Spring 2005)
- Enhanced Bioremediation Technologies (Spring 2000)
- Advancements in In Situ Bioremediation (Spring 2001)
- Bio – State of the Practice (Fall 2007)

https://portal.navfac.navy.mil/portal/page/portal/navfac/navfac_ww_pp/navfac_nfesc_pp/environmental/erb/rits_page/tab5390713

Key Points

- EZVI combines degradation capabilities of two common remediation technologies
  - Zero-valent iron (ZVI)
  - Biodegradation
- EZVI both sequesters and degrades chlorinated volatile organic compounds (CVOCs)
- Microscale and nanoscale iron are suitable for EZVI
- The ZVI provides rapid and immediate degradation and the vegetable oil component of the EZVI emulsion droplet can provide more long-term biodegradation
- Multiple injection technology options are available for application

Presentation Overview

- Technology Overview
- Technology Implementation
- Case Studies
- Other Applications
- Cost
- Summary

– ZVI
  - Chemistry, Applications, Limitations

– nZVI and mZVI
  - Reactivity, Applications, Advantages, Limitations

– EZVI
  - Theory, Chemistry, Applications, Advantages, Limitations

– Application Methods
  - History
  - Advantages, Limitations

ZVI

- ZVI is a strong reducing agent
- ZVI is an accepted technology for degradation of dissolved CVOCs such as PCE and TCE to ethene, as well as metals and pesticides
- ZVI role in degradation:

$$Fe^0 \longrightarrow Fe^{+2} + 2e^-$$

$$2H_2O \longrightarrow 2H^+ + 2OH^-$$

$$2H^+ + 2e^- \longrightarrow H_{2(g)}$$

$$X\text{-}Cl + H^+ + 2e^- \longrightarrow X\text{-}H + Cl^-$$

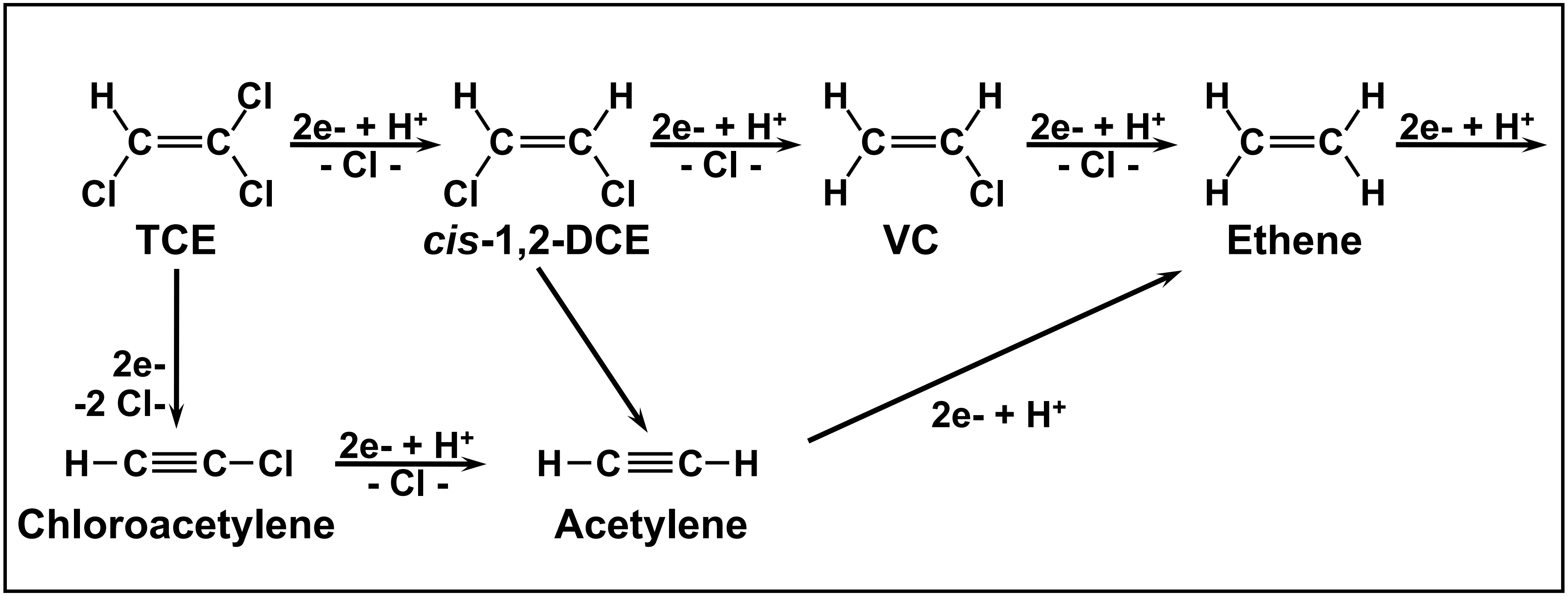
$$C_2HCl_3 + 3H^+ + 6e^- \longrightarrow C_2H_4 + 3Cl^-$$

Essentials for ANY ZVI Treatment

- Highly reduced conditions (-300+ mV)
- Active iron surface
- Contact of iron surface with contaminant
  - Surface-mediated reaction

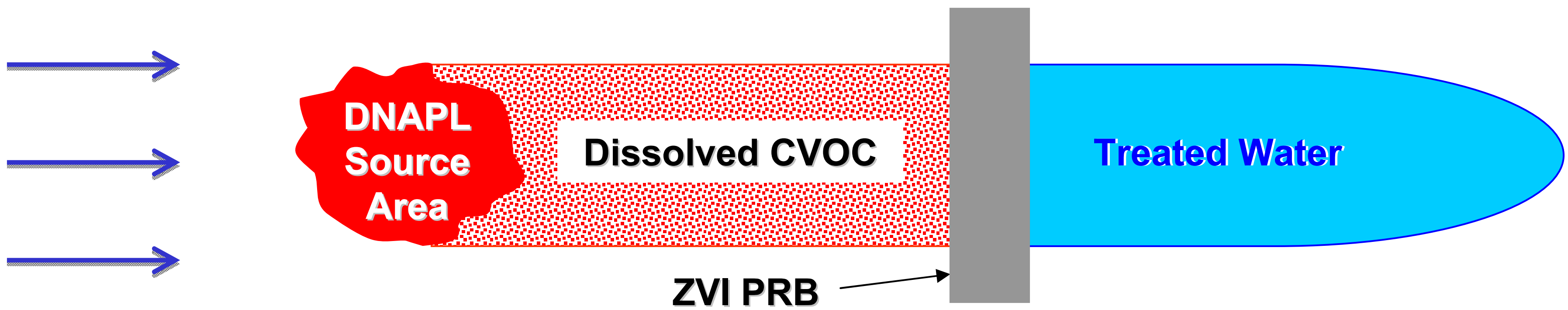
ZVI Chemistry

- Multiple pathways for chlorinated ethene degradation by ZVI
- Surface-mediated reaction but basic chemistry the same regardless of particle size (granular, micro- or nano-scale ZVI)



Common Use of ZVI in Permeable Reactive Barriers (PRBs)

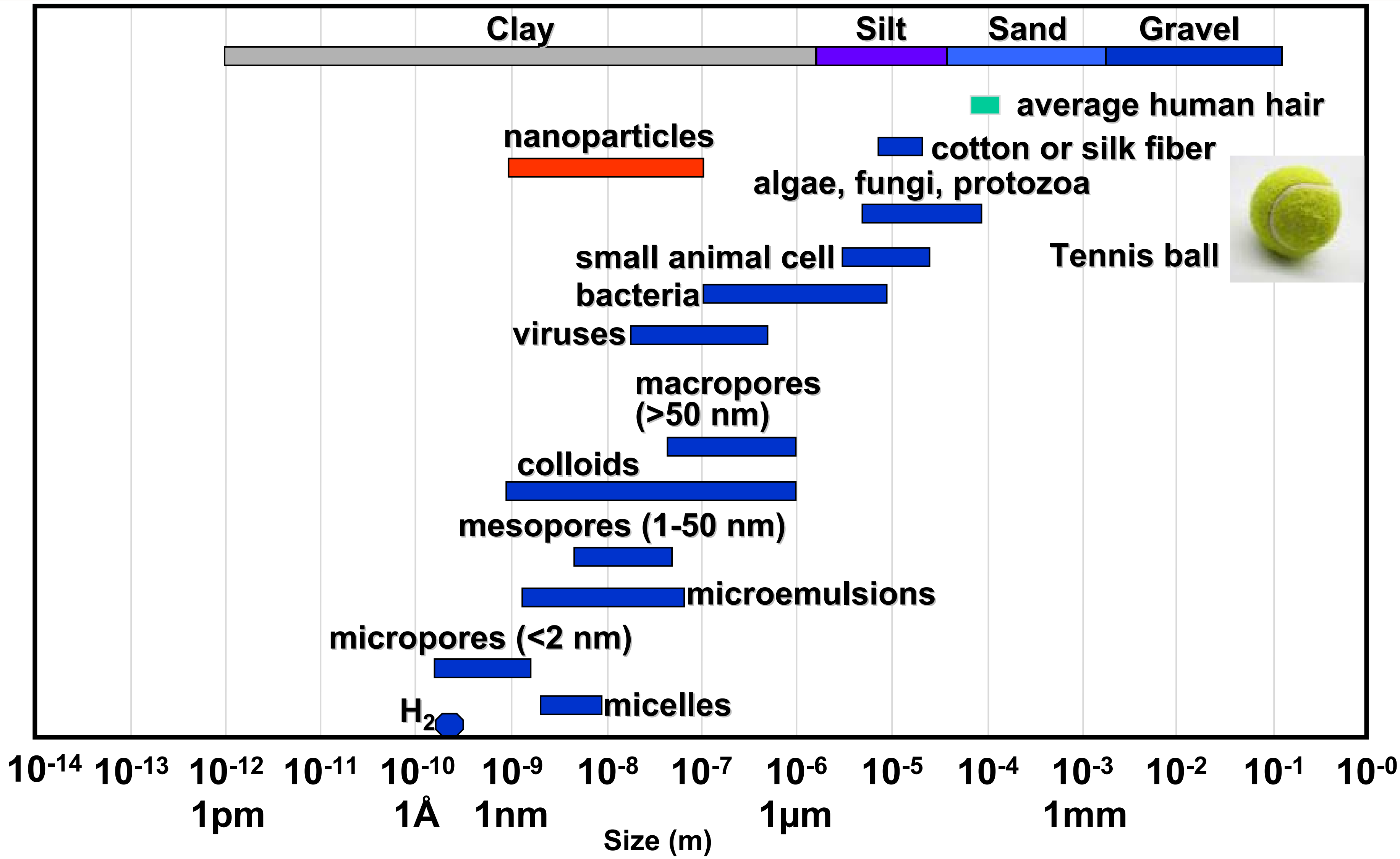
- ZVI (granular) PRBs are effective in treating dissolved CVOCs but:
  - Are dependent on dissolution and transport of CVOCs; and ∴
  - Do little to reduce the clean up time and long-term monitoring costs
- ZVI needs to be in the presence of water to promote reductive dehalogenation
- Injection of ZVI into a DNAPL source zone will only treat the dissolved phase at the edges of the DNAPL



Nanoscale and Microscale ZVI (nZVI and mZVI)

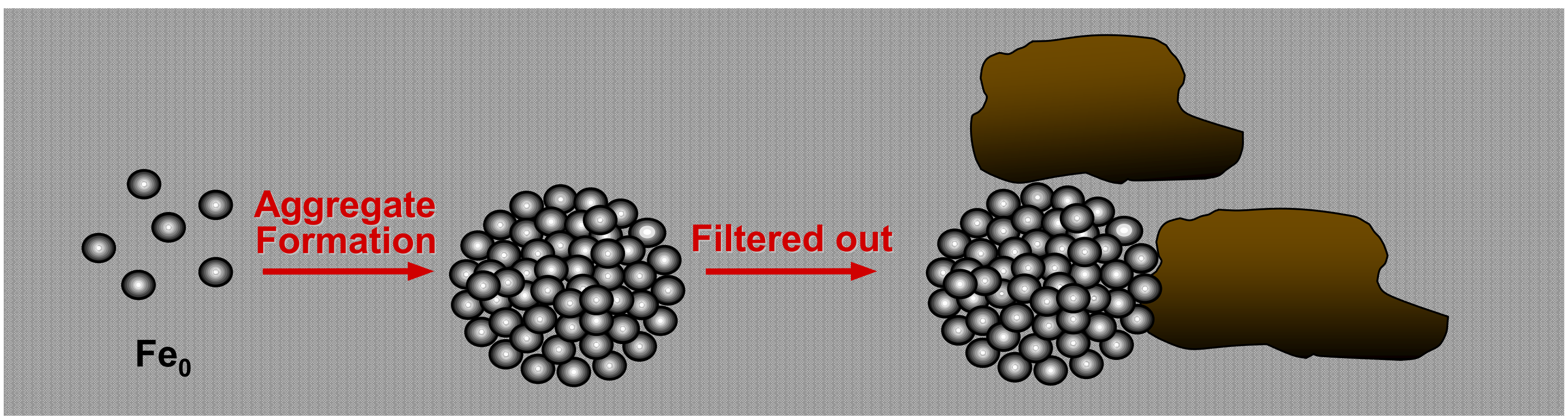
- nZVI particle sizes typically range from 50 to 300 nanometers (nm)
- Surface area of nZVI 30 times greater than granular iron per unit volume (up to 33.5 m^2/g)
- mZVI particle sizes typically range from 1,000 to 3,000 (up to 40,000) nm or 1 to 3 µm
- Large surface area of mZVI and very large surface area of nZVI equals large number of reactive sites for degradation to occur
- 10 to 1,000 times more reactive than granular iron
- However, basically the same chemistry

Nano Particles



nZVI Properties

- Theoretically, nZVI particles are able to travel with groundwater and be transported downgradient of the point of injection
- In reality, magnetic and colloidal properties of nZVI may result in aggregation during storage, handling and once injected into the subsurface
- nZVI can be filtered out by soil such that much of what is injected remains very close to the point of injection



nZVI Properties

- Highly reactive and may be consumed by unwanted reactions (e.g., hydrolysis of water) and/or consumed before degradation is complete
- Iron surface can become passivated and no longer reactive
- Evaluating coatings for nZVI to lessen aggregation & enhance performance
- Need to balance the advantages with the reduction in aggregation and increased mobility with the loss in reactivity

EZVI

- EZVI consists of emulsion droplets containing iron particles in water surrounded by an oil-liquid membrane
- EZVI is composed of food-grade surfactant, biodegradable vegetable oil, water, and ZVI (nano- or micro-scale iron)

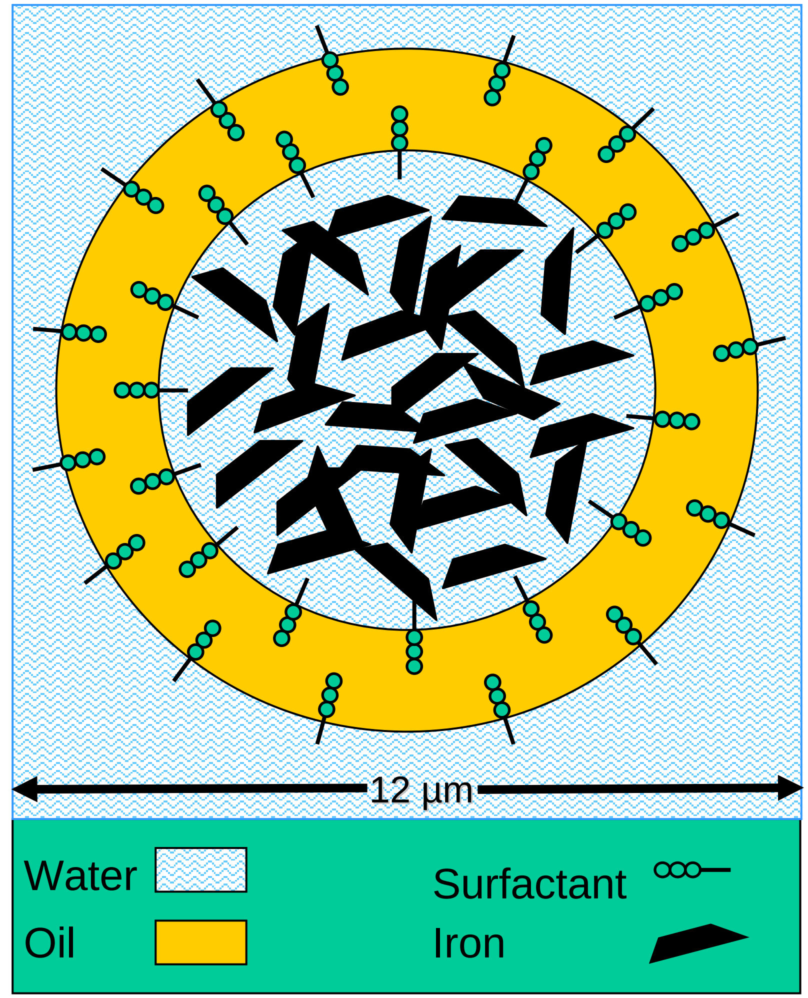


Image of EZVI and DNAPL Contact

- Since exterior oil membrane of emulsion droplets have hydrophobic properties similar to DNAPL, the emulsion is miscible with the DNAPL

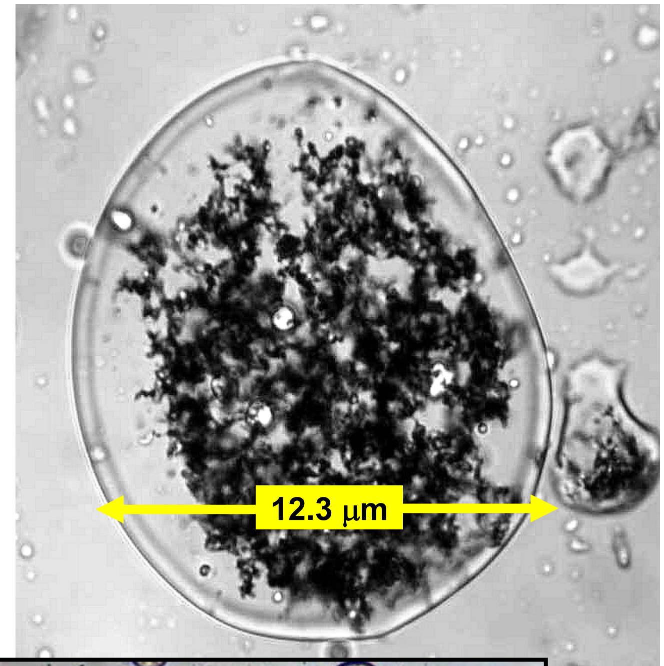
DNAPL
dyed red

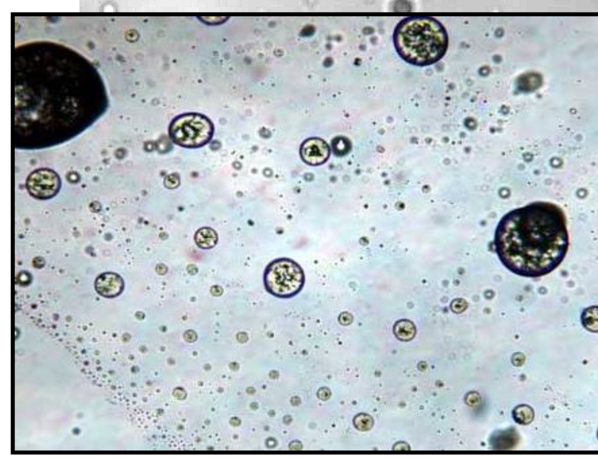
DNAPL
with nano-scale ZVI

DNAPL
with EZVI

EZVI (cont.)

- VOCs in DNAPL diffuse through the oil membrane and are degraded in the presence of the ZVI in the interior aqueous phase
- In addition to abiotic degradation due to iron, EZVI contains vegetable oil and surfactant which will act as a long-term electron donor and promote anaerobic biodegradation
- EZVI featured on a Discovery Channel program on nano technologies

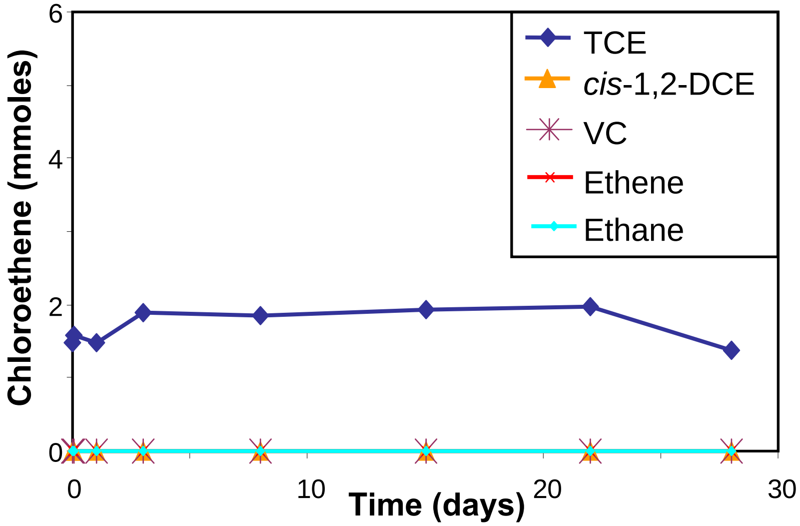




EZVI Laboratory Testing Summary

- Lab tests conducted to evaluate treatment of near saturation dissolved phase concentrations (1,000 ppm) and DNAPL (10 x saturation) using:
  - Controls (active and sterile)
  - Vegetable oil & surfactant (emulsion)
  - Nano-scale zero-valent iron (nZVI)
  - Emulsified zero-valent iron (EZVI)
- Monitor VOCs, DHG and chloride in the water phase of each reactor

EZVI Laboratory Testing

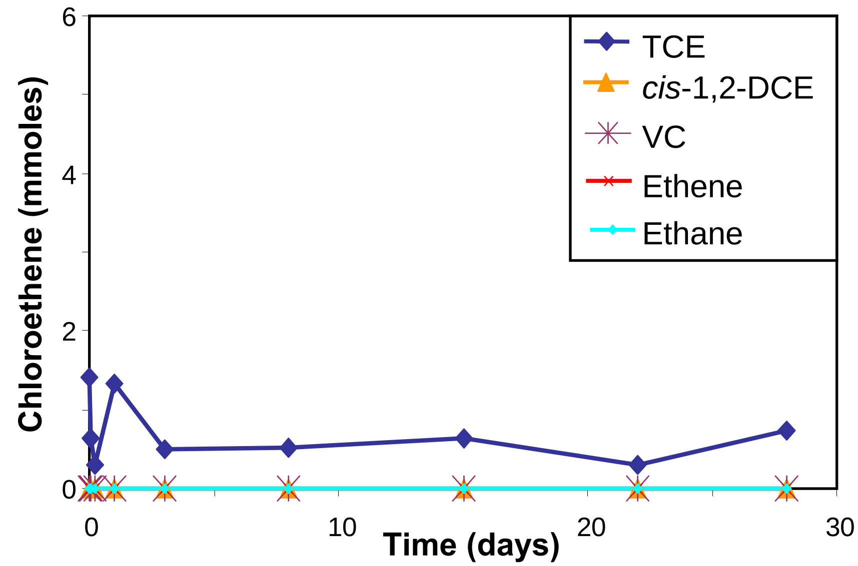


Active Control

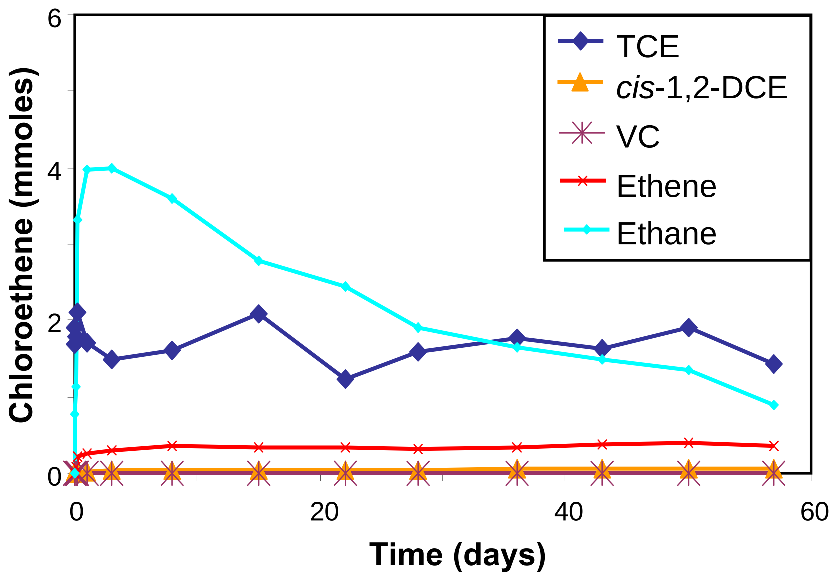
- TCE at saturation concentration
- No degradation by-products observed (no DHG or chloride)

Oil Emulsion Treatment

- TCE stable at ~30% of saturation concentration
- No degradation by-products observed (no DHG or chloride)
- DNAPL sequestered in oil phase – equilibrium concentrations lower than for pure phase DNAPL



EZVI Laboratory Testing (cont.)

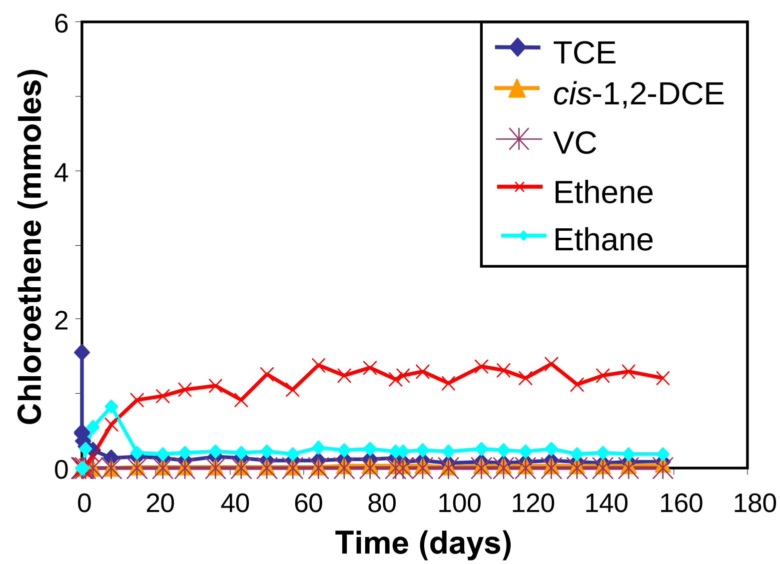


nZVI Treatment

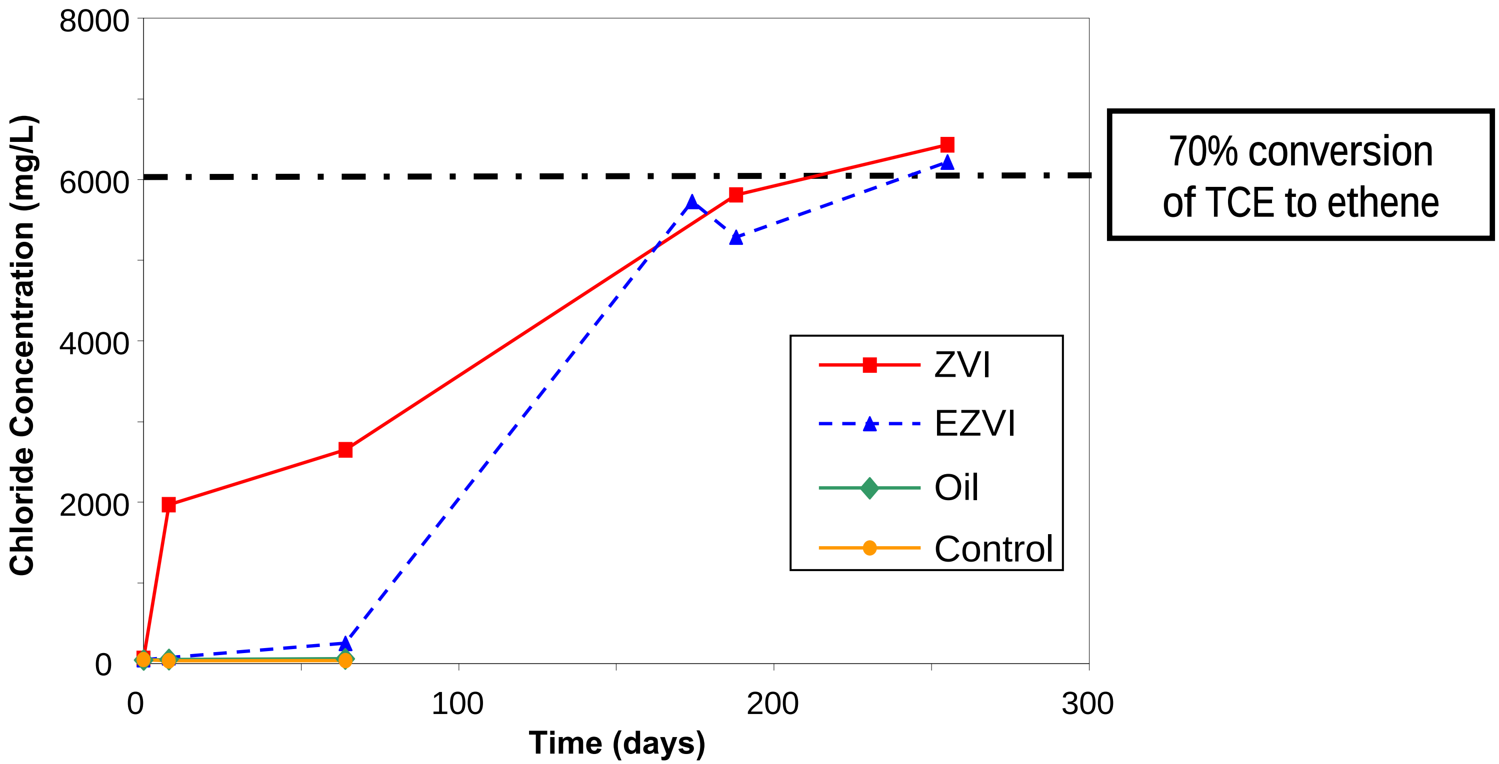
- TCE stable at saturation concentration
- Degradation by-products observed (ethane and ethene)
- Chloride production indicates degradation of ~73% of TCE

EZVI Treatment

- TCE ~10% of saturation concentration and dropping
- Degradation by-products observed (ethane and ethene)
- Chloride production indicates degradation of ~71% of TCE



EZVI Laboratory Testing – Chloride Production with DNAPL



Conclusions of EZVI Laboratory Testing

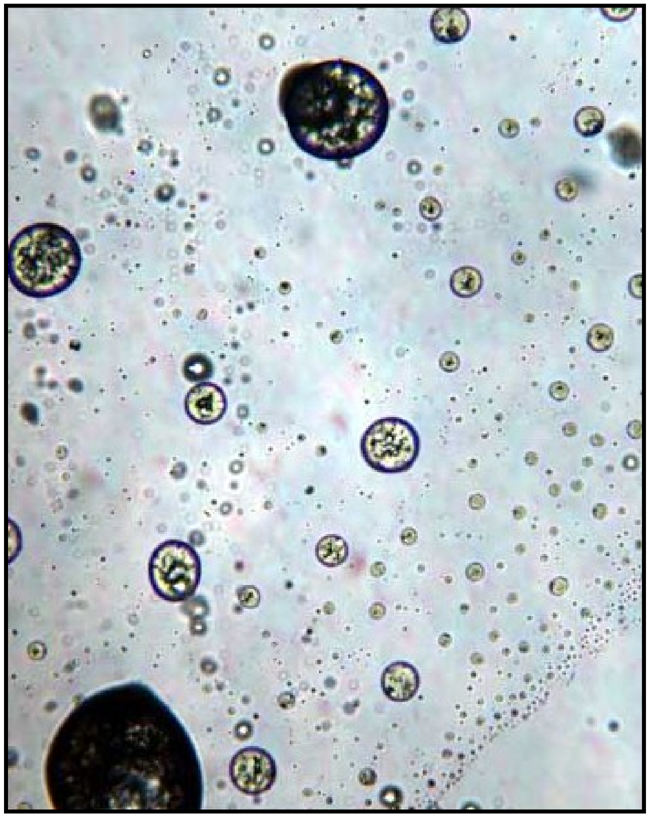
- Veg oil emulsion decreases TCE concentration due to sequestration (no degradation) in test
- nZVI reduces mass of TCE due to treatment but no decrease in aqueous concentration of TCE if DNAPL present (no effect on mass flux)
- EZVI benefits from sequestration due to oil plus degradation due to nZVI
  - Significant decrease in aqueous concentrations (drop in mass flux) greater than with just the oil; and
  - Reduction in mass of TCE

EZVI Application Methods

- Injection
  - Direct injection
  - Pneumatic injection
  - Pressure pulse injection
  - Hydraulic fracturing
- Large diameter auger mixing
- EZVI is a fairly viscous fluid and can be difficult to emplace in the target treatment interval

Application History

- NASA holds the patent for EZVI
- Technology has been successfully commercialized by NASA and has been licensed to 6 companies
- EZVI awarded Invention of The Year and Commercial Invention of The Year by NASA and the Federal Government, and was inducted into the Space Technology Hall of Fame



Application History

State - Location	Year	Volume (gal)	Size of Iron	Primary Contaminant	Soil Type	Injection Method
Central FL - LC34	2002	670	nano	TCE	sand and sandy silt	pressure pulse
TN	2004	1,000	nano and then micro	PCE, TCE	residuum	direct injection
Central FL	2005	62,000	mix - nano and micro	TCE	sand	pneumatic
Southern FL	2005	2,300	mix - nano and micro	TCE	sand	pneumatic
Southern AR	2005	800	mix - nano and micro	EDB	clay	pneumatic
SC	2005	1,400	micro	PCE,TCE,TCA	saprolite	direct injection
IL	2005-2006	920	micro	PCE	clayey silt	pneumatic
OH	2005-2006	1,840	micro	PCE	sandy silt	pneumatic
SC - Parris Island	2006	750	nano	PCE	sandy silt, clay and peat	direct injection and pneumatic
Central FL	2006	6,000	micro and a mix of nano and micro	TCE	sand	direct injection
MA	2006	600	mix - nano and micro	PCE, TCE	fractured bedrock	gravity flow
TX	2006	1,840	micro	CT	sandy silt	pneumatic
NC	2006	1,800	micro	TCE	residuum	direct injection
LA	2006 & 2008	2,300	micro	CT	silty vadose zone	pneumatic
Central FL	2007	3,000	mix - nano and micro	TCE	sandy	direct push hybrid
IL	2007-2008	10,800	micro	TCE	clayey silt	pneumatic

EZVI Advantages and Limitations

Advantages

- *In situ* treatment of DNAPL source areas is possible thereby shortening time for closure
- Immediate sequestration provided by oil and degradation provided by ZVI
- Significant decrease in mass flux due to VOCs partitioning into oil
- Long-term biodegradation provided by oil, bioaugmentation can enhance biodegradation
- Complete reduction to non-toxic end products possible
- ZVI provides treatment of chemicals which may inhibit biodegradation (e.g., Freon)
- Minimal labor and waste disposal

Limitations

- Not generally cost-effective for dispersed plumes
- Cost of nZVI material itself can be high – can use mZVI instead
- Due to viscosity can be hard to inject and difficult to get EZVI to target treatment zone
- Well-characterized source zone needed

Presentation Overview

- Technology Overview
- Technology Implementation
  - Conceptual Site Model (CSM)
  - Site Characterization
  - Design
  - Performance Monitoring
- Case Studies
- Other Applications
- Cost
- Summary

Conceptual Site Model

- Developed based on the results of site characterization
- Necessary to determine applicability of EZVI and appropriate design parameters for implementation
- Design of EZVI application may be inappropriate or insufficient if the conceptual model is incorrect or incomplete

Factors that Need to be Determined for Applicability of EZVI

- Site Characteristics
  - Hydrogeology
  - Geology and depth of target treatment interval
  - Geochemistry
  - Contaminant type and distribution (source zone delineation)
- Site Constraints
  - Site access restrictions
- Remedial Objectives
  - Regulatory requirements
  - Other remedial objectives

Site Characterization

- Additional characterization in the target treatment area may be necessary:
  - Geology of targeted treatment zone
  - Horizontal and vertical distribution of contamination
  - Groundwater flow characteristics
  - Presence of underground obstacles
  - Presence of indigenous microorganisms
    - Consider bioaugmentation when injecting EZVI to boost the biodegradation component

Choosing Injection Technologies

Site Characteristic			Injection Technology to Consider			
			Direct Injection	Pneumatic Injection	Pressure Pulse Injection	Large Diameter Augers
Geology		homogeneous	Consider	Consider	Consider	Use caution
		heterogeneous	Consider	Consider	Consider	Consider
		homogeneous	Use caution	Consider	Use caution	Consider
		heterogeneous	Use caution	Consider	Use caution	Consider
		highly fractured	Use caution	Consider	Use caution	Probably not applicable or may be very expensive to use
		few fractures	Probably not applicable or may be very expensive to use	Consider	Probably not applicable or may be very expensive to use	Probably not applicable or may be very expensive to use
Depth	0-10 ft		Consider	Use caution	Use caution	Consider
	10-50 ft		Consider	Consider	Consider	Consider
	50-100 ft		Consider	Consider	Consider	Probably not applicable or may be very expensive to use
	>100 ft		Consider	Consider	Consider	Probably not applicable or may be very expensive to use
Size	<0.5 acres		Consider	Use caution	Consider	Consider
	0.5 to 1 acre		Consider	Consider	Consider	Consider
	>1 Acre		Probably not applicable or may be very expensive to use	Consider	Probably not applicable or may be very expensive to use	Probably not applicable or may be very expensive to use

Consider

Use caution

Probably not applicable or may be very expensive to use

Design and Remediation Management Considerations

- The EZVI application should be implemented in the source zone or area of highest contaminant concentrations
- Consider bioaugmentation to enhance complete degradation
- Other elements of design include:
  - Extent of treatment necessary (volume)
  - Dosage of EZVI (may be much greater than stoichiometric ratio Fe/TCE = 1.3/1; safety factor and ability to distribute effectively)
  - Injection method
  - Radius of influence to determine location and number of injection points (located in source area)

❖ Consider injecting maximum of 30% of available pore space and no less than 10% so that it can be properly distributed throughout target treatment area

nZVI / mZVI Issues = EZVI Issues

- Iron Surface Passivation
  - Minimize storage time of nZVI / EZVI
  - J-I-T Manufacturing either on- or off-site
- Significant variability of properties of nZVI and mZVI
  - Therefore, all EZVI is not the same
  - Obtain QA/QC documentation from manufacturer or test iron and even EZVI prior to use

Performance Monitoring

- Compliance Monitoring
  - Regulatory monitoring requirements
  - Groundwater samples upgradient and downgradient of treatment zone
- Performance Monitoring
  - Used to determine short-term and long-term effectiveness of treatment technology
  - Groundwater samples include:
    - Contaminant levels
    - TOC, ORP, pH
    - Manganese, iron, chloride, sulfate
    - Dissolved hydrocarbon gases (e.g., ethene, ethane, methane)
  - Soil samples include
    - Contaminant levels
    - Visual confirmation of EZVI presence

Soil and Groundwater Samples

Presentation Overview

- Technology Overview
- Technology Implementation
- Case Studies
  1. Launch Complex (LC) 34
  2. ESTCP – Parris Island, SC
  3. Patrick Air Force Base, FL
- Other Applications
- Cost
- Summary

Case Study #1 – Launch Complex 34

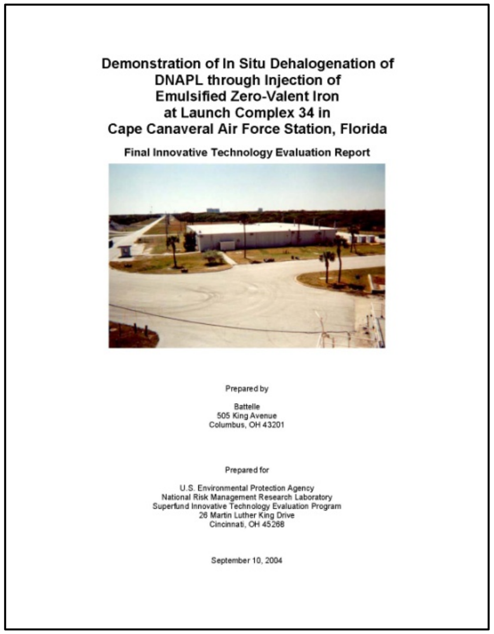
- Demonstration conducted at NASA's LC34, Cape Canaveral, FL
- Launch Complex 34 was used as a launch site for Saturn rockets from 1960 to 1968
- Demonstration conducted by Geosyntec and University of Central Florida and independently evaluated by EPA Superfund Innovative Technology Evaluation (SITE) Program (Battelle SITE contractor)

Launch Complex 34

- Pilot test area was inside of a building and was 15 ft by 10 ft
- Performance evaluation based on GW mass flux and TCE mass in pre- and post-treatment soil cores
- Monitored changes in CVOCs in:
  - Groundwater
    - 5 depth intervals, 2 upgradient and 2 downgradient wells; and
  - Soil cores
    - 8 depth intervals, 6 locations

Papers and Reports

- ES&T published special issue on nanotechnology
- NASA and Geosyntec co-authored paper in this issue on the EZVI Field Demonstration
- Quinn et al., 2005. Field Demonstration of DNAPL Dehalogenation Using Emulsified Zero-Valent Iron. Environ. Sci. Technol. 2005, 39, 1309-1318.
- Battelle conducted an independent evaluation for EPA of the EZVI demonstration at LC34



Demonstration of In Situ Dehalogenation of DNAPL through Injection of Emulsified Zero-Valent Iron at Launch Complex 34 in Cape Canaveral Air Force Station, Florida

Final Innovative Technology Evaluation Report

Prepared by

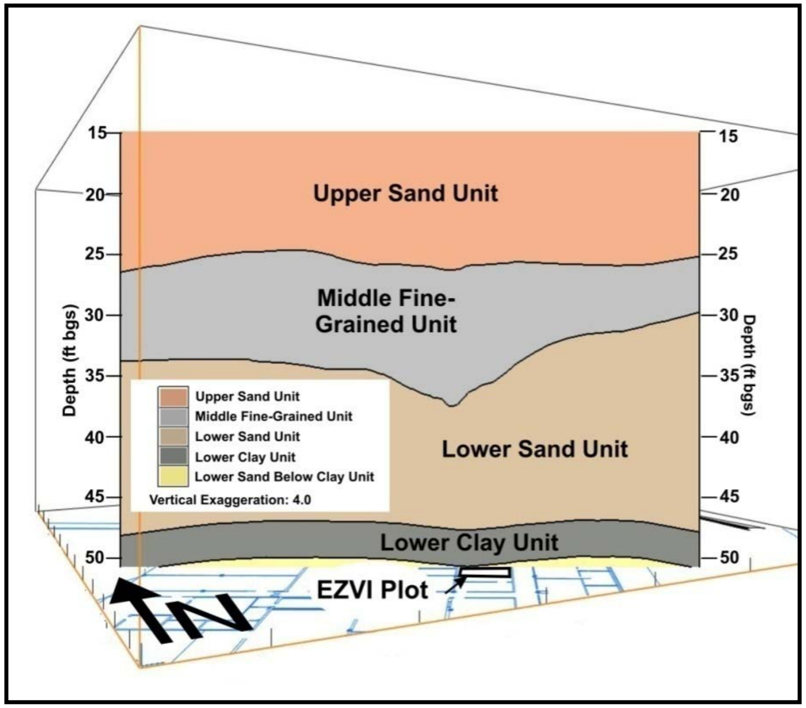
Battelle
505 King Avenue
Columbus, OH 43201

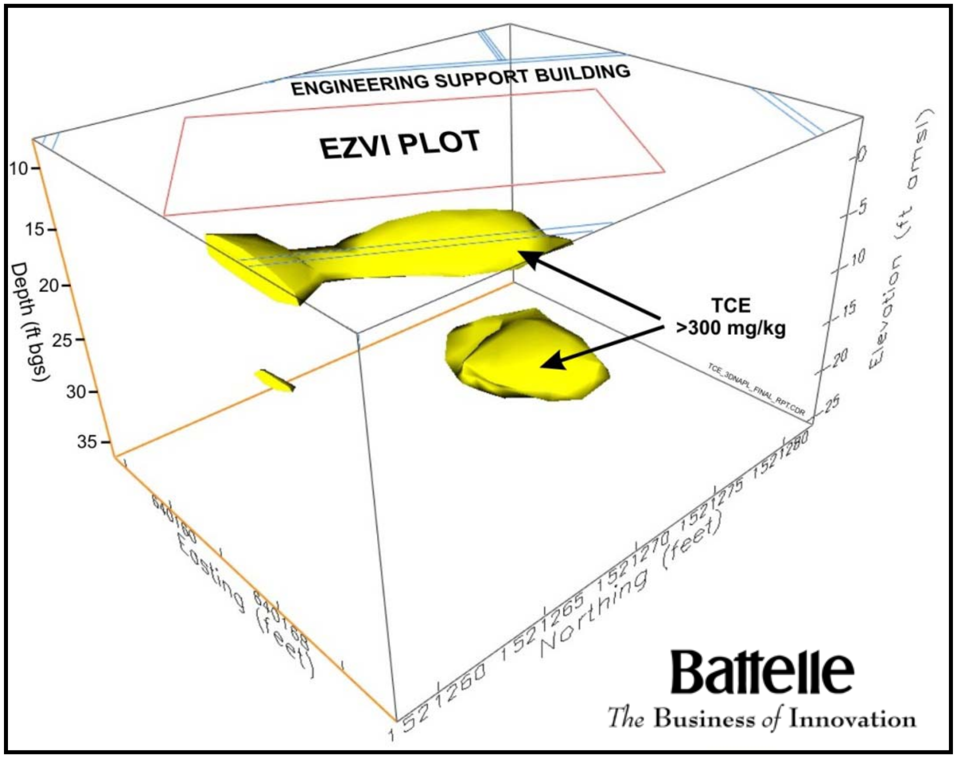
Prepared for

U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Superfund Innovative Technology Evaluation Program
26 Martin Luther King Drive
Cincinnati, OH 45268

September 10, 2004

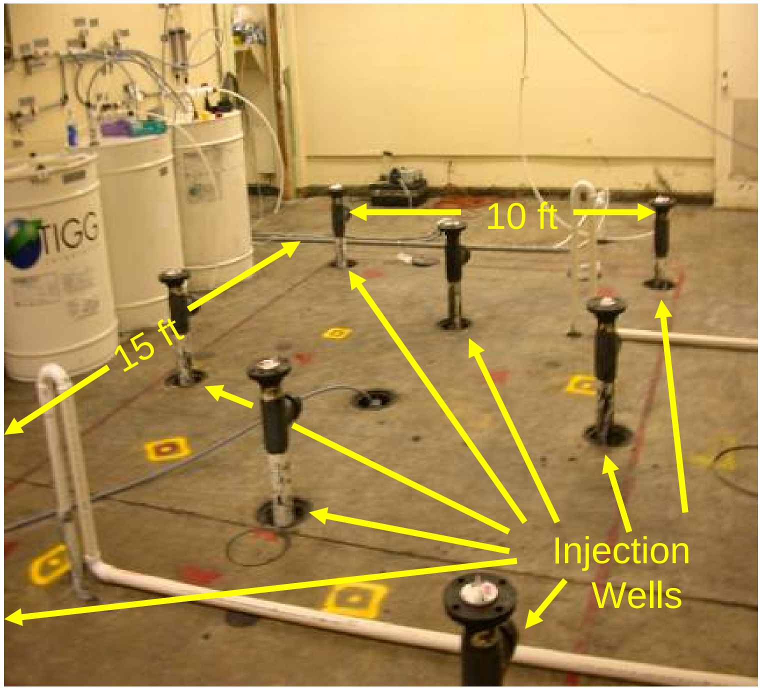
Site Geology and Contaminant Distribution





Technology Implementation

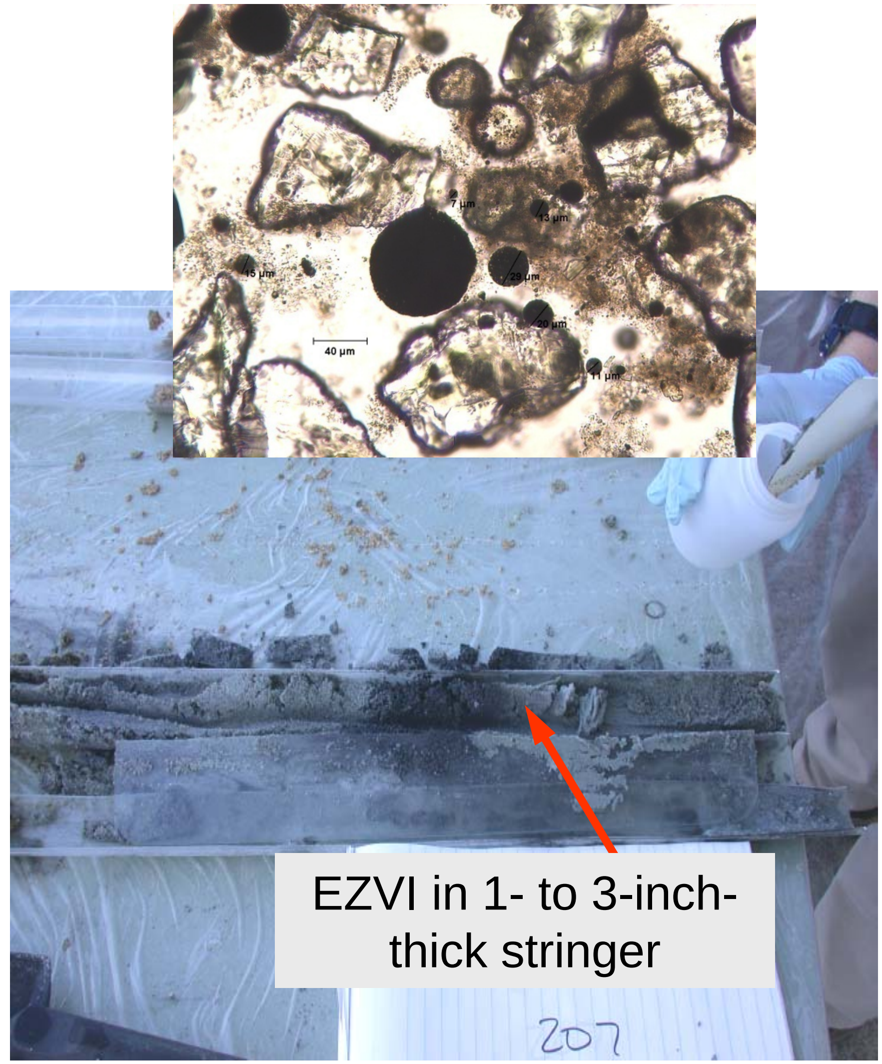
- EZVI injected in 8 injection wells using pressure pulse technology
- Injection wells along edge of plot directed inwards
- Injection wells in center were fully screened
- Injection at 2 discrete depth intervals in each well



EZVI Injection Setup within Pilot Test Area

Results – Soil

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



Results – Groundwater

- Groundwater Samples:
  - Significant reduction (60 to 100%) of TCE in target depths
  - Reduction of 56% in the Mass Flux
  - 18 months after injection, groundwater concentrations indicate that long term degradation due to bioremediation is ongoing
  - Elevated *cis*-1,2-DCE and vinyl chloride (VC) suggest biodegradation due to oil as an electron donor may also be significant

Results – Injection Technology

- EZVI was found in soil cores within 5 feet of the injection wells at 10 to 26 ft bgs – well above target injection depth of 16 to 24 ft bgs
- Evidence of upward movement of EZVI although EZVI is well dispersed in sediments

Recommendations and Follow-on Work

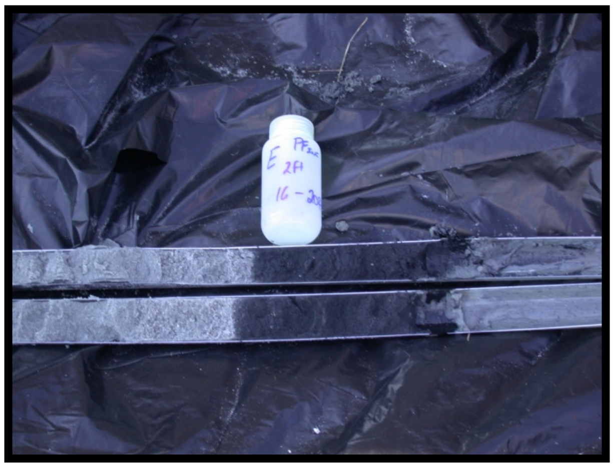
- Promising results at LC34, but needed to determine:
  - How to control placement of EZVI in subsurface
  - Evaluate the contribution of the abiotic and biological components of the degradation
- ESTCP project to evaluate contribution of abiotic and biological components and further evaluate EZVI (Case Study #2)

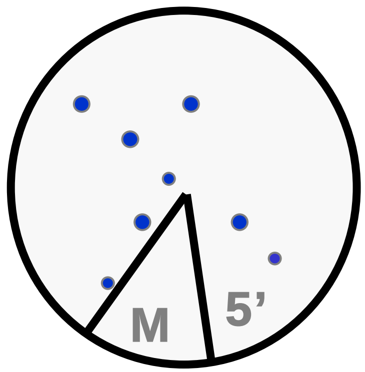
Follow-on Work – Injection Testing

- Evaluation of four different injection techniques to improve ability to deliver EZVI to source zone
  - Direct injection
  - Pneumatic injection
  - Hydraulic fracturing/injection
  - Pressure pulse technology with different injection tools

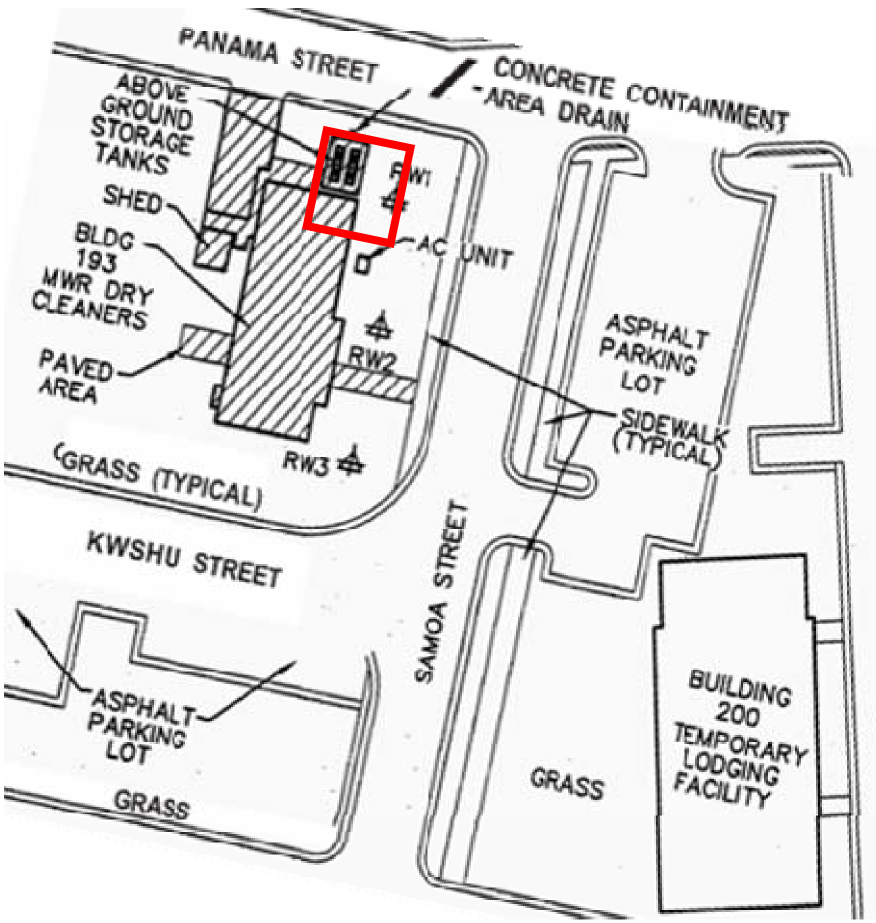
Follow-on Work – Injection Testing (cont.)

- All four technologies were able to inject EZVI without damaging the emulsion structure
- Pneumatic and direct injections had the best control over placing EZVI in target treatment interval
- Pneumatic had best radius of influence and mixing — felt that with more volume to inject could have gotten greater than the target 5 ft





Case Study #2 – ESTCP – Parris Island SC



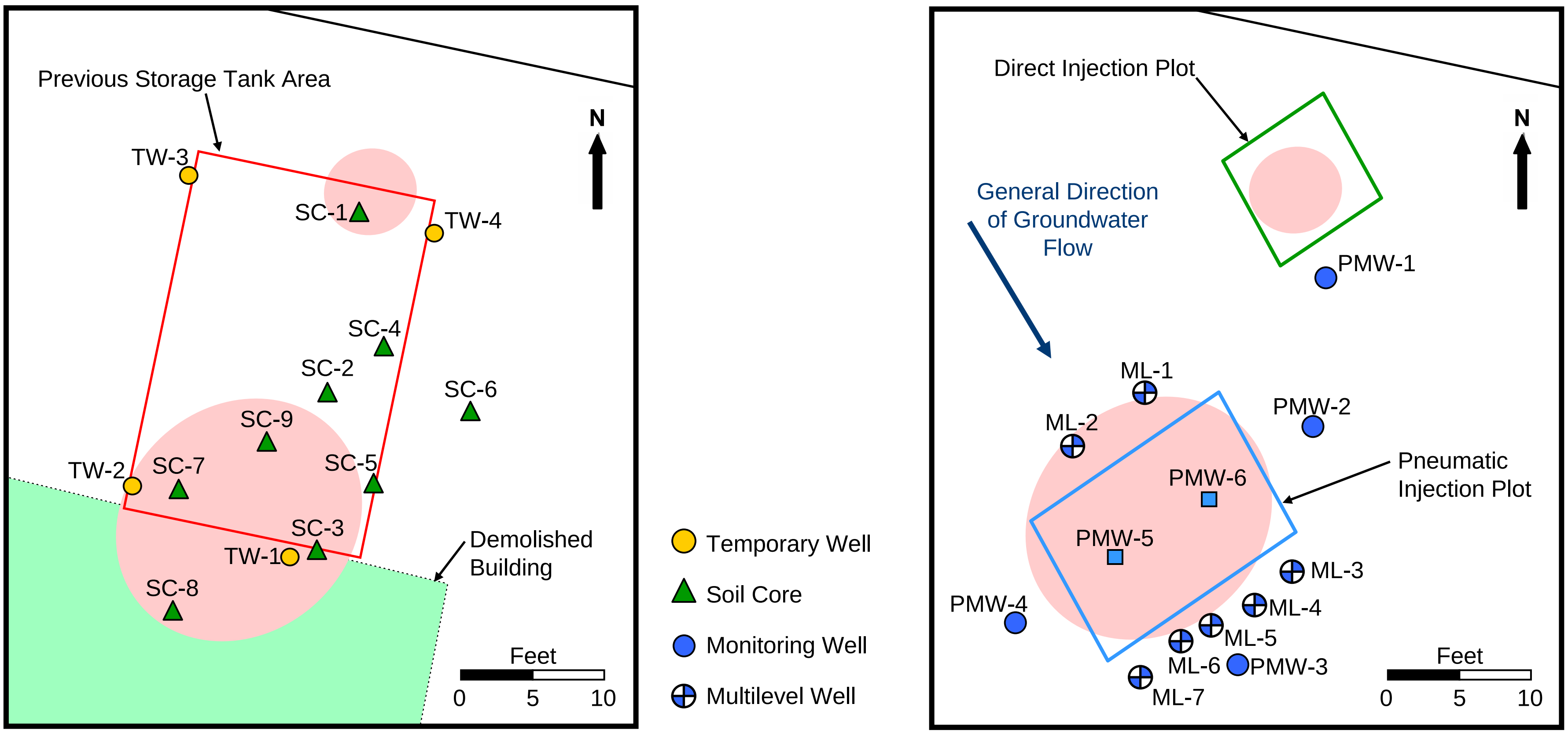
- Environmental Securities Technology Certification Program (ESTCP) project ER-0431
- Site 45, Parris Island MCRD, SC
- Former dry cleaning facility
- Buildings have been torn down
- Source areas located around former aboveground and belowground storage tanks

Papers and Reports

- Spring 2006, Remediation Journal Paper on EZVI Laboratory Evaluation
  - O'Hara, S., Krug T., Quinn, J., Clausen C., and Geiger, C. 2006. Field and Laboratory Evaluation of the Treatment of DNAPL Source Zones Using Emulsified Zero-Valent Iron. *Remediation Journal*, Wiley Periodicals, Inc. Spring 2006.
- Final Reports for ESTCP for this project (ER-0431) are due in the fall of 2009
  - Technical Report
  - Cost and Performance Report

Site Geology and Contaminant Distribution

- Well-characterized site with number of wells, soil cores and cone penetrometer testing (CPT)/ membrane interface probe (MIP) borings
- Wells installed in July 2006 to target the source areas



Manufacturing EZVI

- EZVI was made on-site by mixing nanoscale iron (Toda), corn oil, surfactant and water in drums using top-mounted industrial mixer

  - EZVI can be made on-site or purchased from one of the licensed manufacturers

    http://nasaksc.rti.org/ezvi.cfm

Manufacturing EZVI (cont.)

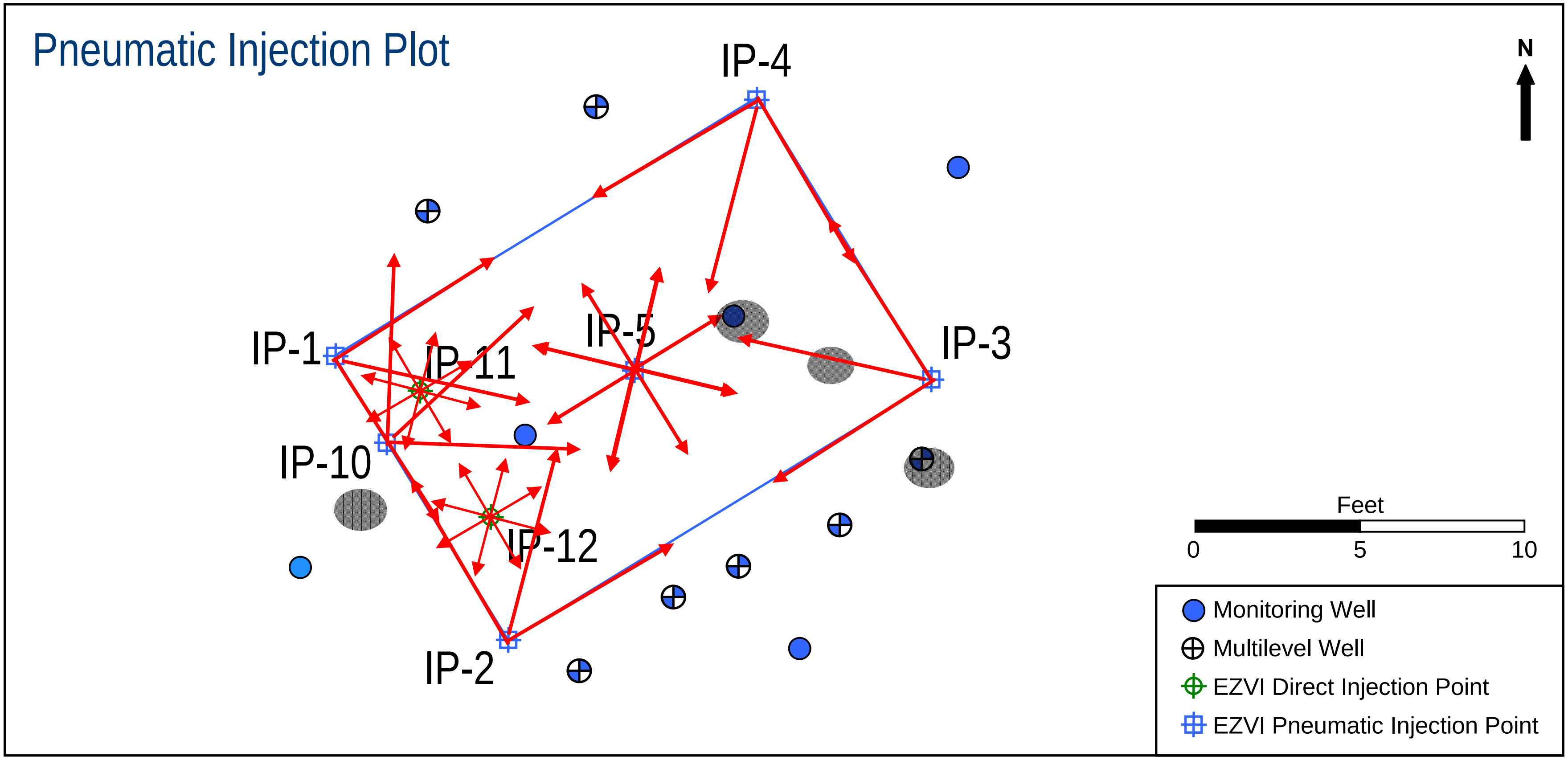
- EZVI was made in 55-gal drums that the nZVI was shipped in and then pumped from mixing drums into injection tanks

Technology Implementation – Pneumatic

Pneumatic Injection Plot

- 575 gal EZVI injected into 8 locations between 7 and 19 ft bgs (2 locations supplemented with direct Injection)
- During injections, monitored injection pressure, pressure distribution in subsurface, ground heave, and looked for EZVI at ground surface (daylighting)

Pneumatic Injection Plot

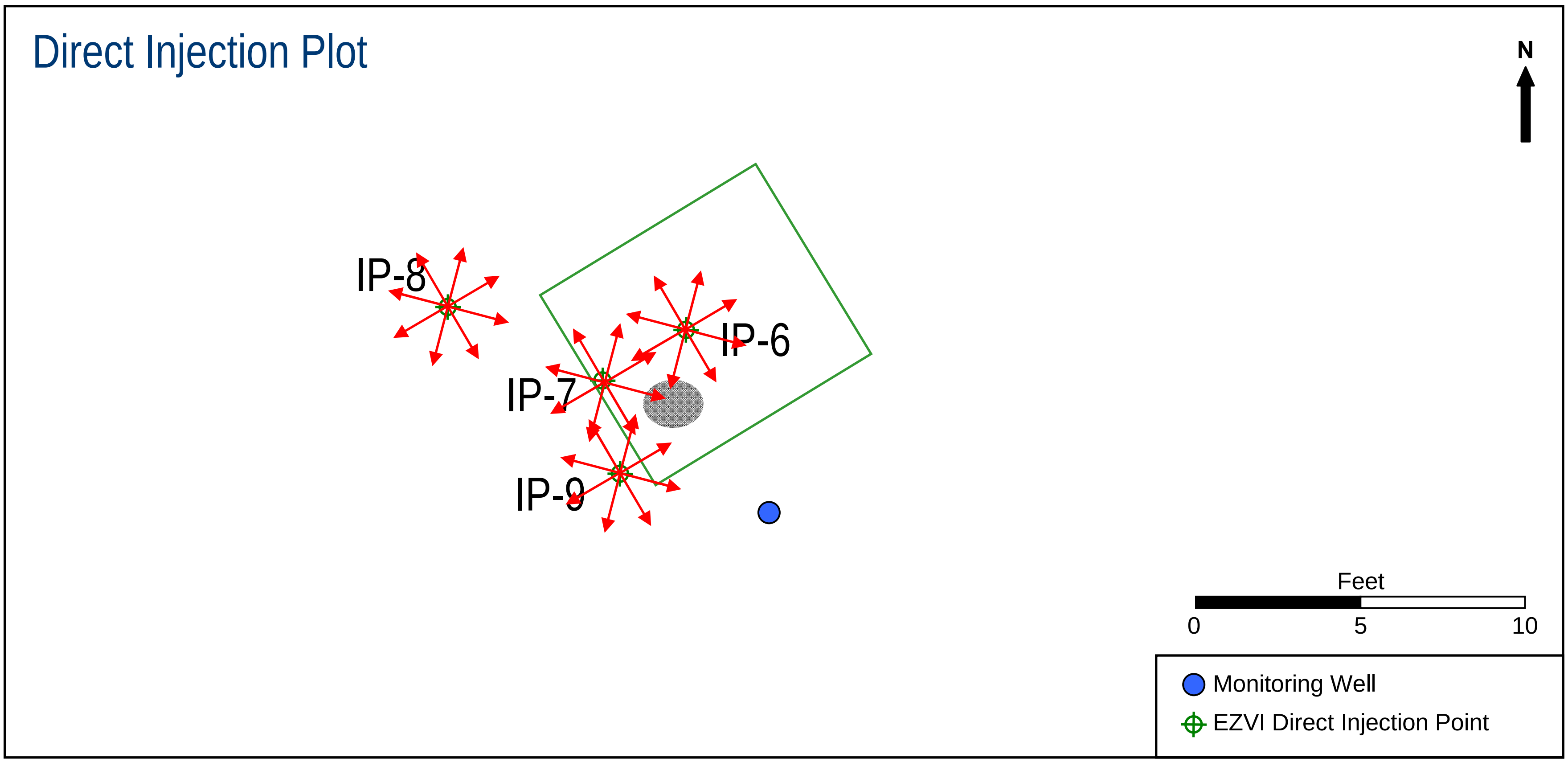


Technology Implementation – Direct Push

Direct Injection Plot

- 150 gal EZVI injected into 4 locations between 6 and 12 ft bgs
- During injections, monitored injection pressure and looked for EZVI at ground surface (daylighting)

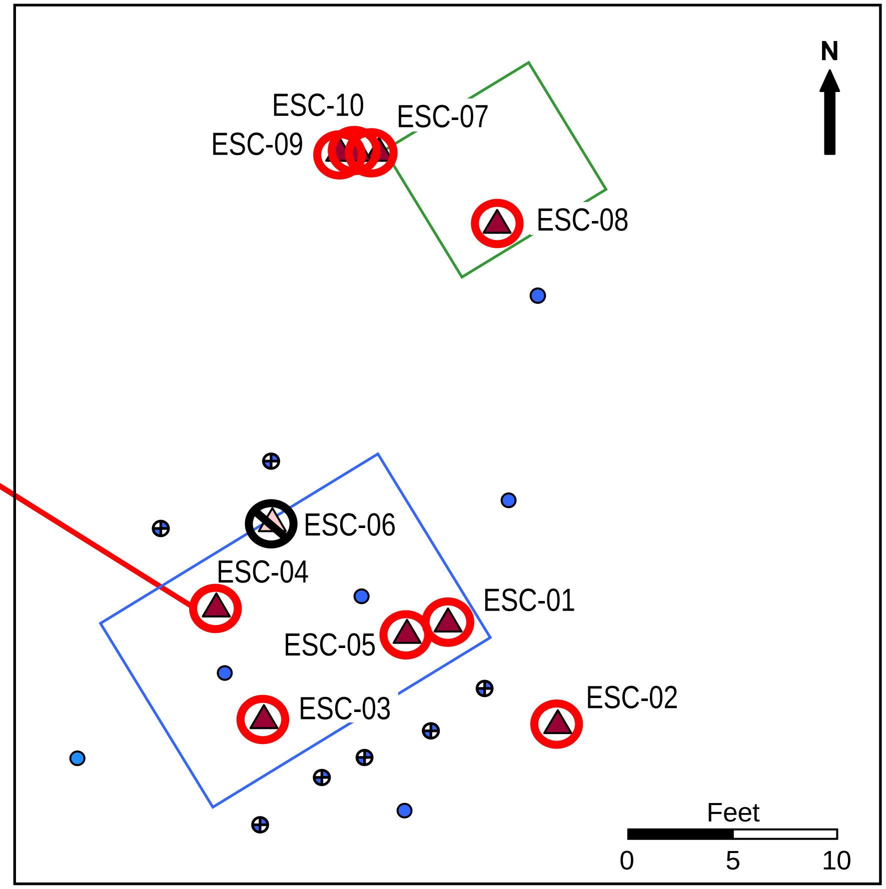
Technology Implementation – Direct Push



Soil Cores – Distribution

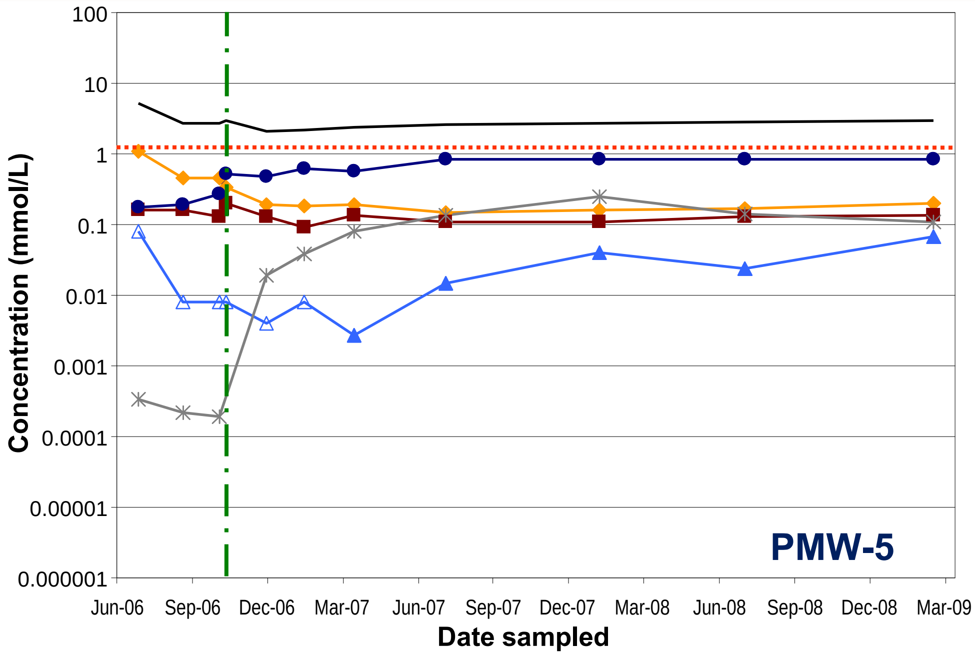
- Cores collected to evaluate ability of injection technologies to distribute EZVI evenly over target treatment intervals

Sand Saturated with EZVI

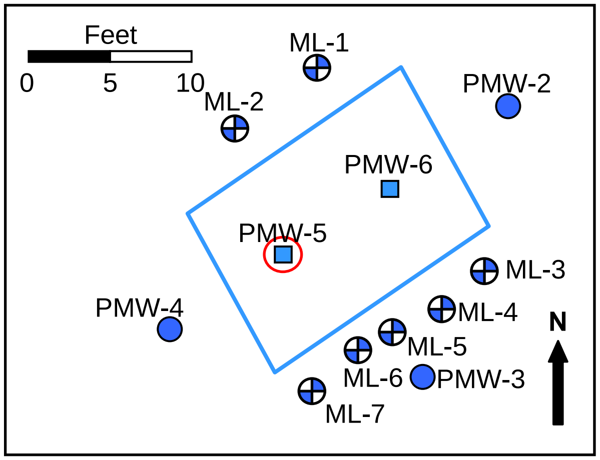


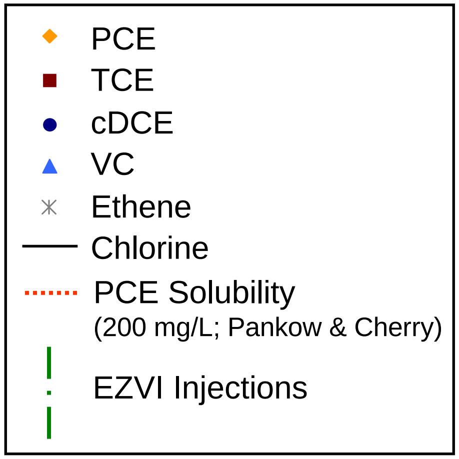
- EZVI in all cores but one (ESC-06)

Results – Groundwater VOC Trends: Wells with DNAPL in Pneumatic Injection Plot



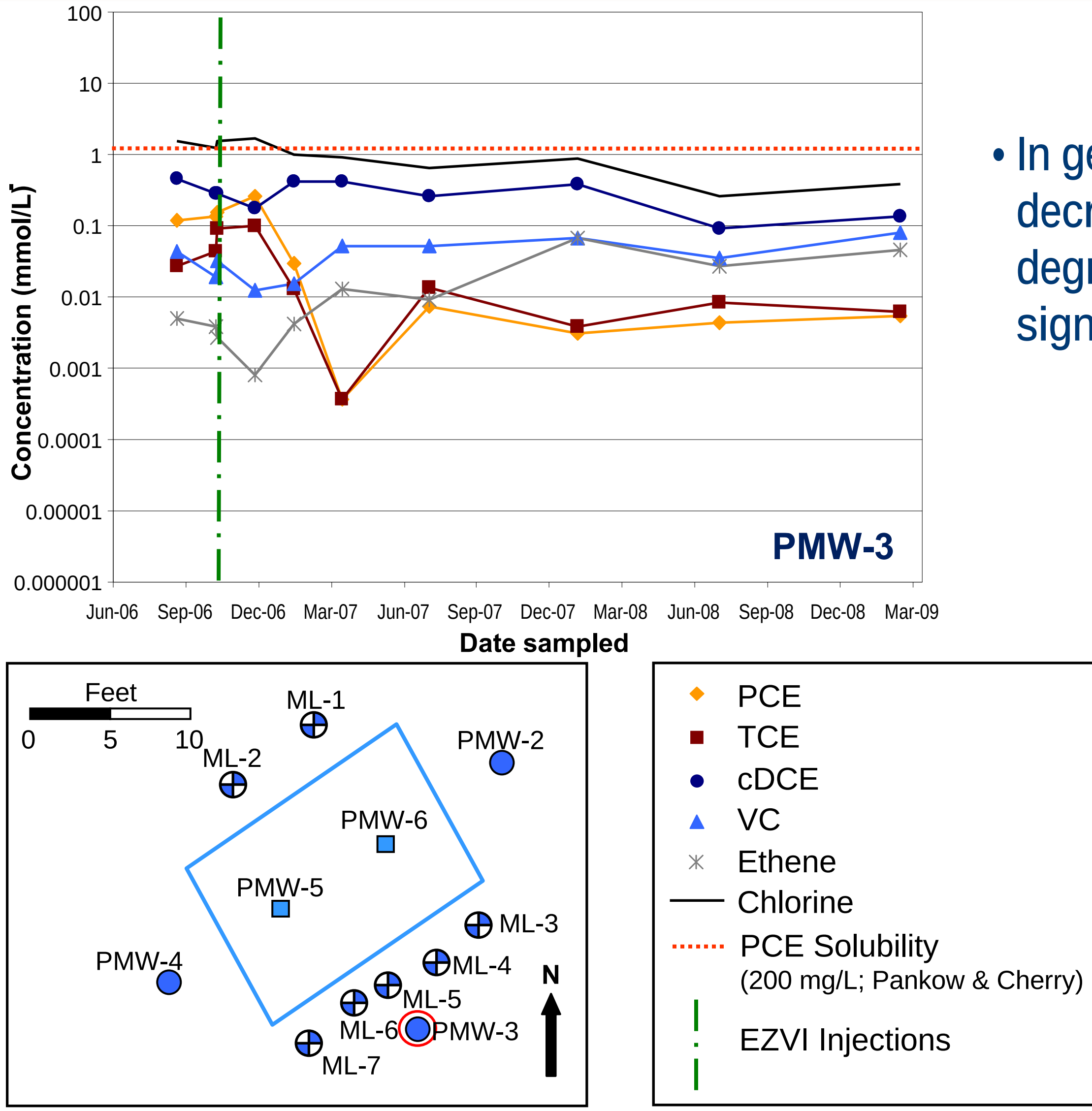
- PMW-5 shows continued presence of DNAPL although significant production of ethene in PMW-5 indicates that degradation is ongoing in the area





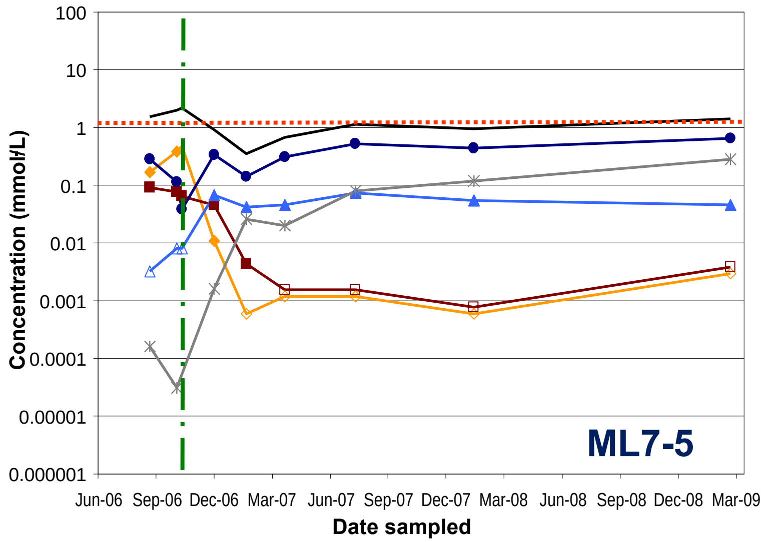
Open symbol indicates non-detects

Results – Groundwater VOC Trends: Downgradient Well from Pneumatic Injection Plot

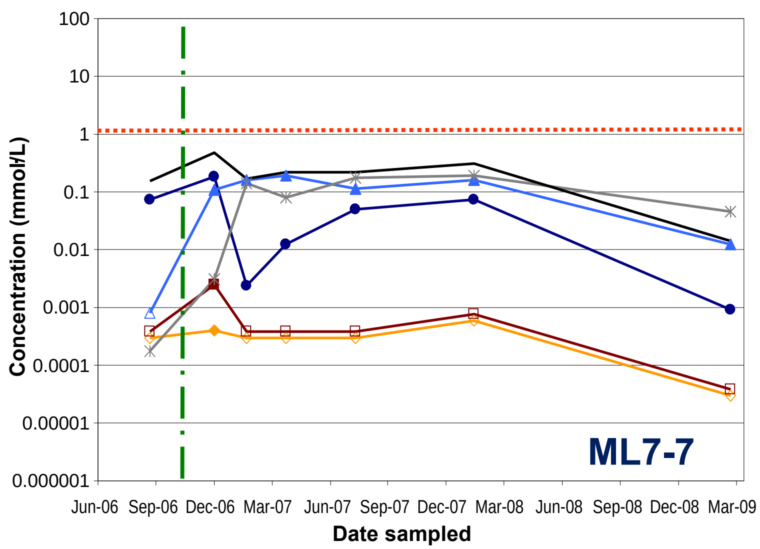


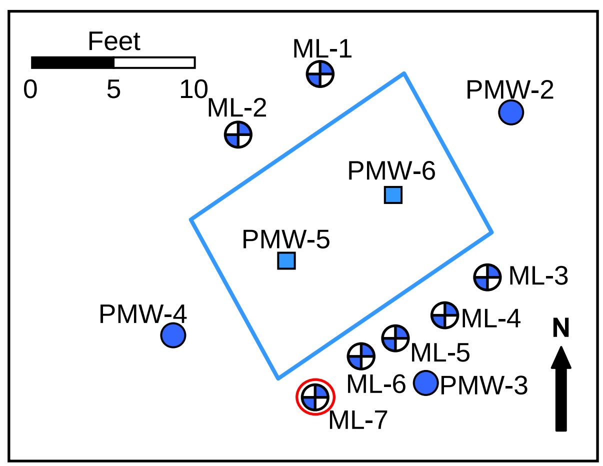
- In general, downgradient wells show decrease in PCE/TCE with increase in degradation products including significant increases in ethene

Results – Groundwater VOC Trends: Downgradient wells in Pneumatic Injection Plot



- Downgradient wells show decrease in PCE/TCE with increase in degradation products including significant increases in ethene





- PCE
- TCE
- cDCE
- VC
- Ethene
- Chlorine
- PCE Solubility (200 mg/L; Pankow & Cherry)
- EZVI Injections

Open symbol indicates non-detects

Results – Injection Technology

- EZVI daylighted in both Pneumatic and Direct Injection test plots

Pneumatic Injection Plot
(daylighting around ML-3 pad, downgradient of plot and from old MIP locations)

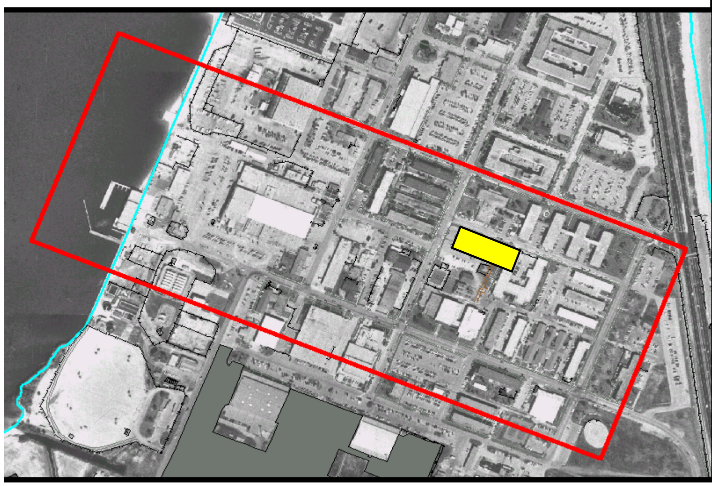
Direct Injection Plot
(daylighting possibly from old soil core location)

Summary and Conclusions

- In general, downgradient wells show decrease in PCE/TCE with increase in degradation products including significant increases in ethene
- Upgradient wells and PMW-5 show continued presence of DNAPL although significant production of ethene in PMW-5 indicates that degradation is ongoing in the area
- DNAPL now being pumped from some wells where DNAPL was previously absent, indicating that some of the DNAPL is mobile
- Difficulty in getting EZVI evenly distributed in this small area due to shallow application and short-circuiting up existing boreholes

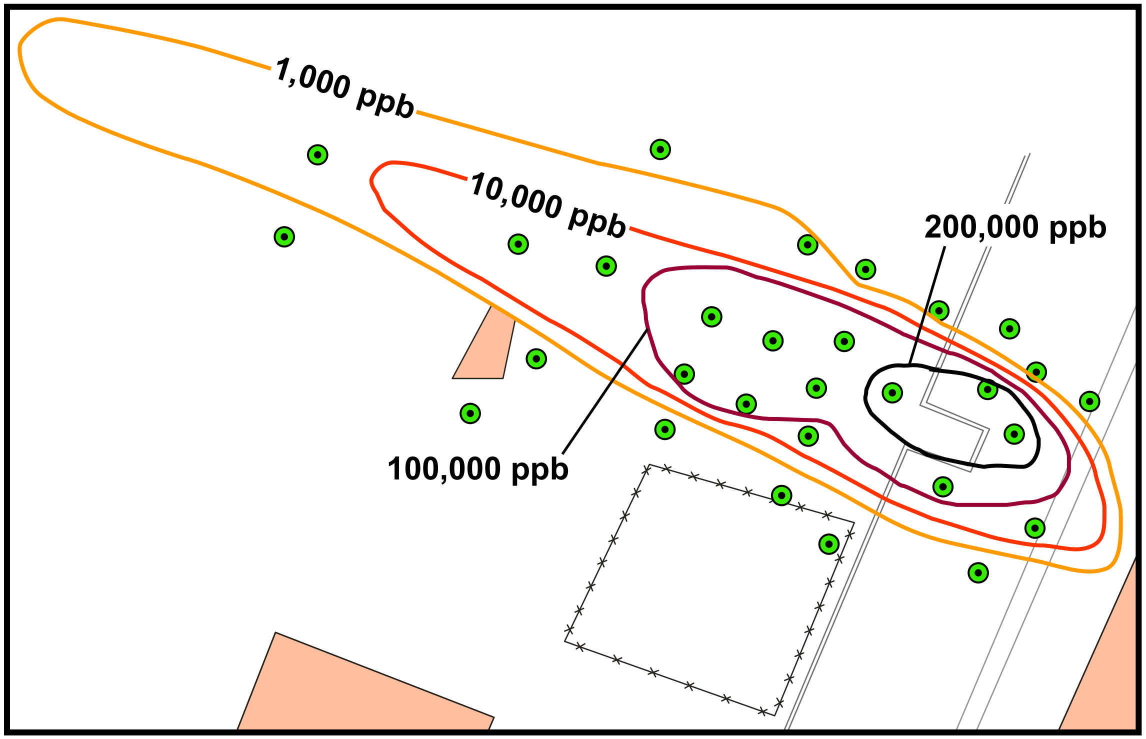
Case Study #3 – Patrick Air Force Base, Florida

- Two apparent source areas, one near Building 533 and one at Building 313
- Past operations (1940s through the 1960s) resulted in releases of trichloroethene (TCE)
- TCE and its breakdown products 1,2-Dichloroethene (DCE) and vinyl chloride (VC) affect groundwater in an area about 600 feet wide by 1,500 feet long

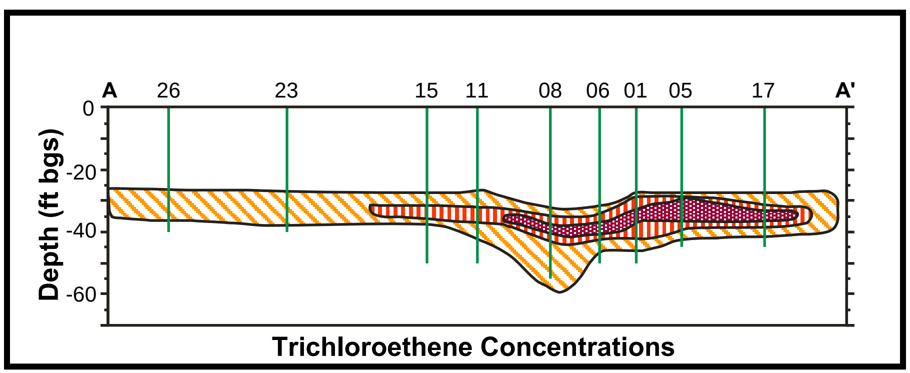


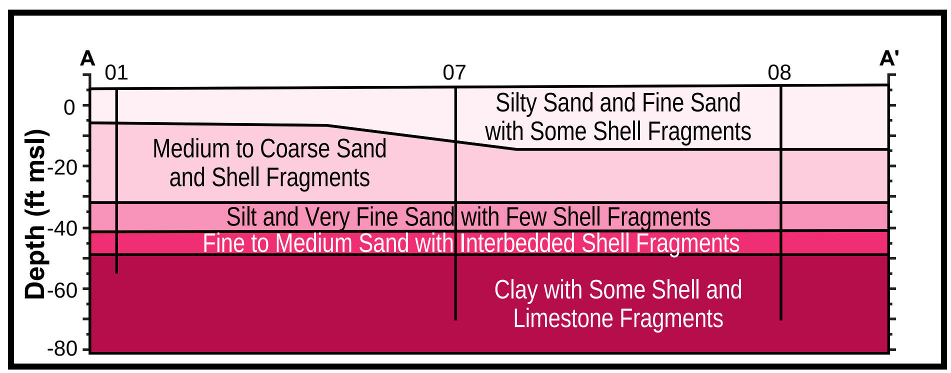
Information on this case study provided by H. Faircloth, Core Engineering & Construction, Inc. and U.S. Air Force, Patrick Air Force Base, FL

Baseline Concentrations



- TCE, *cis*-DCE, VC in groundwater
- TCE up to 350 ppm
- Focus remediation on source area





Approach

- Inject EZVI in source area
- Inject straight vegetable oil in plume area downgradient of source as electron donor
- Co-injection of KB-1 (dechlorinating bacteria) in the source area and in plume

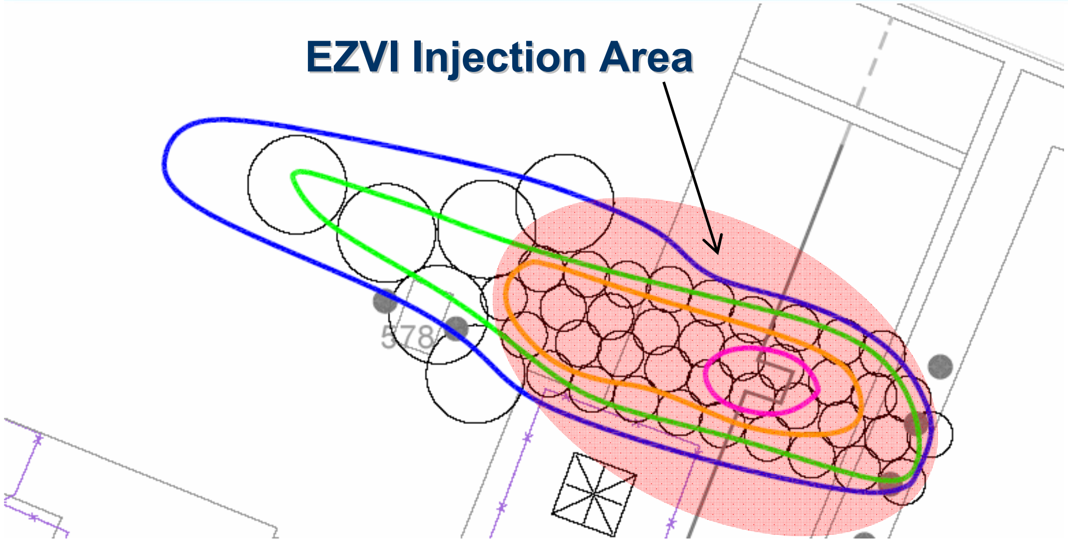
Approach (cont.)

- EZVI injected with pneumatic fracturing/pneumatic injection process in the 100 ppm TCE contour, between 25 and 45 ft bgs (~5,400 ft^2)
- Radius of influence (ROI) = 7 ft (36 injection points)
- KB-1 injection after EZVI injection – direct push rig injecting the KB-1 a couple of days following EZVI injection with pneumatic injection rig

  * EZVI provided by Applied Science & Advanced Technologies, Inc. (ASAT) of Baton Rouge, LA (purchased pre-made and shipped to site)

  * Injections done by Pneumatic Fracturing, Inc.

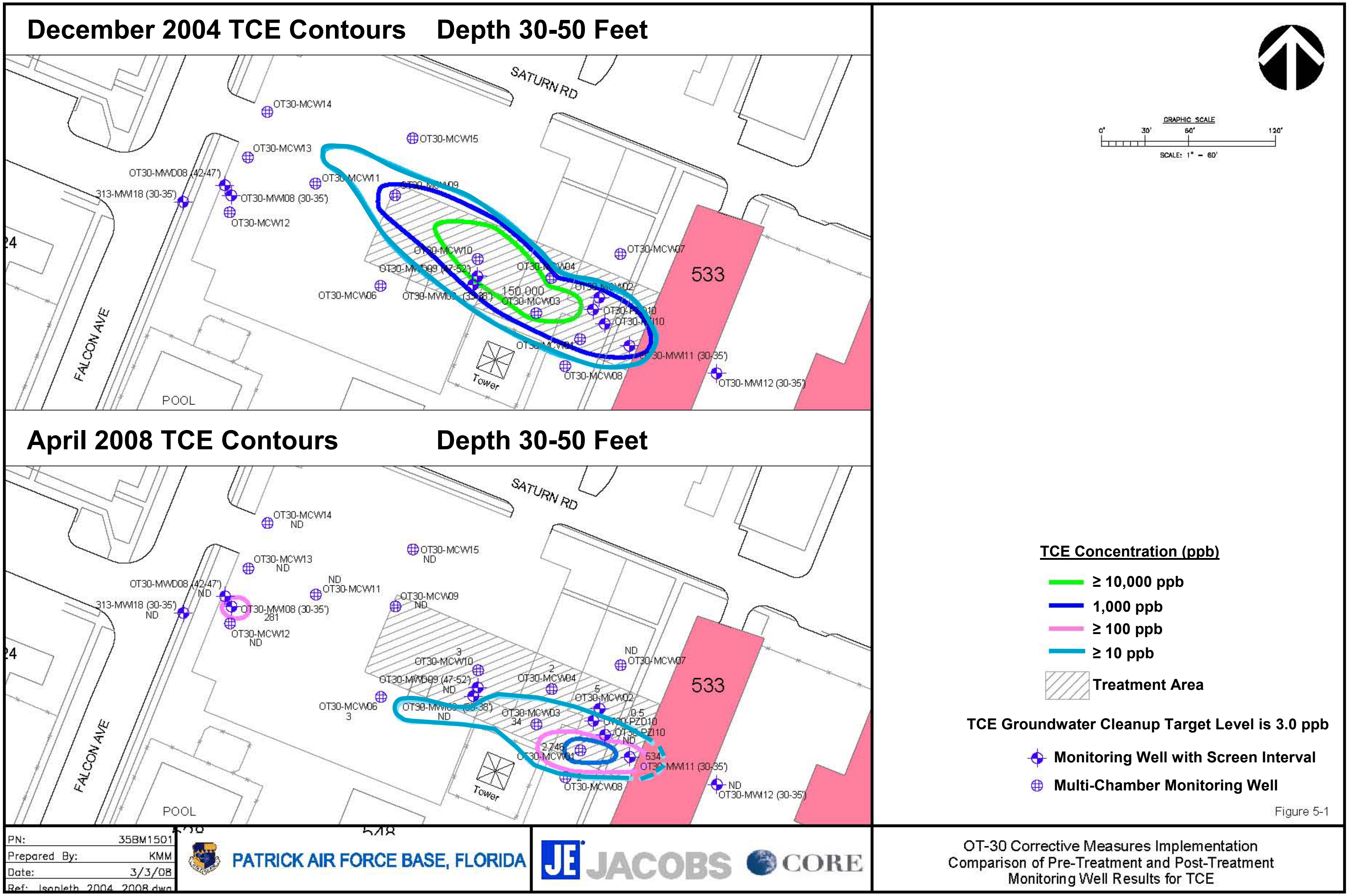
Injection Design



- N_2 used to fluidize formation
- N_2 used as a carrier fluid
- Co-Injection process

- Bottom up injections
- 1 ft. intervals
- 4 injections/interval at most points
- 2 injection/interval at perimeter points

Rotating injection nozzle


December 2004 TCE Contours
Depth 30-50 Feet
April 2008 TCE Contours
Depth 30-50 Feet
SATURN RD
FALCON AVE
POOL
Tower
533
OT30-MCW14
OT30-MCW13
OT30-MCW15
OT30-MCW11
OT30-MCW09
OT30-MWD08 (42-47')
OT30-MW08 (30-35')
313-MW18 (30-35')
OT30-MCW12
OT30-MCW10
OT30-MWD09 (47-52')
OT30-MCW06
OT30-MCW04
OT30-MCW07
OT30-MCW02
OT30-MCW03
OT30-PZD10
OT30-PZI10
OT30-MW11 (30-35')
OT30-MW12 (30-35')
OT30-MCW08
150,000
ND
281
2,748
534
GRAPHIC SCALE
0'
30'
60'
120'
SCALE: 1" = 60'
TCE Concentration (ppb)
≥ 10,000 ppb
1,000 ppb
≥ 100 ppb
≥ 10 ppb
Treatment Area
TCE Groundwater Cleanup Target Level is 3.0 ppb
Monitoring Well with Screen Interval
Multi-Chamber Monitoring Well
Figure 5-1
PN: 35BM1501
Prepared By: KMM
Date: 3/3/08
Ref: Isopleth_2004_2008.dwg
PATRICK AIR FORCE BASE, FLORIDA
JE JACOBS
CORE
OT-30 Corrective Measures Implementation
Comparison of Pre-Treatment and Post-Treatment
Monitoring Well Results for TCE

Lessons Learned

- Shipping/Handling EZVI:
  - Tanker truck shipment is effective for large volume sites
  - On-site storage tanks need to be considered
  - If planning to hold EZVI for > 10 days should have stirring capability to offset separation/compaction/viscosity issues (only in large volume containers 5,000 gallons and larger)
- Injection of EZVI:
  - Inconsistency of product viscosity caused variation in pumping times, nitrogen requirements and potentially impact on ROI
  - Daylighting due to improperly abandoned wells or unknown well locations

Presentation Overview

- Technology Overview
- Technology Implementation
- Case Studies
- Other Applications
  - Modified EZVI Applications
  - Leveraging EZVI Applications
- Cost
- Summary

Modified EZVI Applications

- mZVI versus nZVI to make EZVI
  - Both work well although the mZVI EZVI is less stable over longer period of time and this must be taken into account if transporting pre-made EZVI to site for injection versus making on site
- Co-injection of ZVI and vegetable oil
  - Some groups have been experimenting with co-injection of nZVI and emulsified vegetable oil (EVO) rather than mixing two at surface
- Different emulsification techniques
  - Research into using different surfactants, different mechanical emulsification techniques to make a less viscous EZVI which will be theoretically be easier to emplace in subsurface

http://www.serdp.org/Research/upload/ER_FS_1487.pdf

Leveraging EZVI Applications

- Co-injection or follow-on injection of bacteria to enhance biodegradation component of EZVI
- Applications for co-mingled plumes or sources where either ZVI or bioremediation on its own wouldn't work
  - Metals (abiotic)
  - VOCs (abiotic and biological)
  - Perchlorate (biologic degradation)

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Cost Analysis

The primary factors affecting treatment costs include:

- High reagent cost (e.g., nZVI versus mZVI)
- Size of the contaminated zone
  - Incentive to reduce source footprint through more-detailed characterization
- Field implementation restrictions such as drilling and infrastructure
- Monitoring requirements
- Cleanup goals

Costs for nZVI

Iron Powder

- $1/lb
- ~ 1 m^2/kg
- ~ 1 m^2/dollar

Nano Iron

$25/lb

~ 25,000 m^2/kg

~ 1,000 m^2/dollar

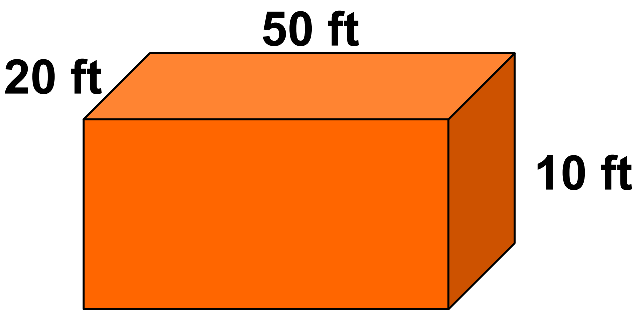
Data for actual remediation costs is scarce…

Cost of EZVI

- Cost of nZVI and to lesser extent mZVI is what drives cost of EZVI
- Cost of other ingredients are minimal (up to $6/gal)
- The cost of manufacturing the EZVI can be higher if you need large volumes that can't easily be made on site
  - ~$10/gallon if made on site for mZVI EZVI
  - $27/gallon for nZVI EZVI made on site

Iron Product	Supplier	Cost
Nanoscale ZVI	Toda America	$26-$34/lb, depending on quantity
Microscale ZVI (40,000 nm)	ARS Technologies	$1-$1.70/lb
Microscale ZVI (up to 3,000 nm)	BASF	$4/lb
Granular Iron (comparison only, can't use to make EZVI)	Peerless Metal Products, Master Builders	$0.40/lb

EZVI Cost Scenario



10,000 cf impacted by DNAPL

30% porosity = 3,000 cf

TREAT 10% to 30% of porosity =

300 to 900 cf EVZI

EZVI (on-site, gal) 2,250 to 6,750

Small mZVI ($10/gal) = $22,500 to $ 67,500

nZVI ($25/gal) = $56,250 to $168,750

If large volume of EZVI required – Negotiate Costs!

Cost of Injection

- Dependent on site geology, size of treatment area
- Rough costs for injection with pneumatic could be around $650/injection lift (targeting roughly 10 ft radius of influence over a 4 ft depth interval)
- Direct Injection methods costs are approximately $255/injection point (assumes five injection points a day)

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Summary and Conclusions

- Emulsified Zero-Valent Iron (EZVI) both sequesters and degrades CVOCs
- Microscale and nanoscale iron are suitable for EZVI
- The vegetable oil component of the EZVI emulsion droplet can provide a bio-polishing of the site
- Multiple injection technology options are available

Additional Information Resources

- NASA-Kennedy Space Center's information on EZVI: http://nasaksc.rti.org/ezvi.cfm ← **Excellent Resource**
  - Technology description
  - Laboratory Studies
  - Case Studies
  - Licensed vendors
- Fact Sheet on ESTCP Project ER-0431: http://www.estcp.org/Technology/ER-0431-FS.cfm
- Fact Sheet on SERDP Project ER-1487 http://www.serdp.org/Research/upload/ER_FS_1487.pdf

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- 2003 ACS Paper
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- Presentation at Battelle in Monterey, May 2008
  - O'Hara, S., Krug T., Watling, M., Quinn, J., Ruiz, N., Su, C., Puls, R., 2008. Field Evaluation of the Treatment of DNAPL Source Zones Using Emulsified Zero-Valent Iron. Platform presentation at the Sixth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA. May 19-22, 2008.