

Field Evaluation of the Treatment of DNAPL Using Emulsified Zero-Valent Iron (EZVI)

Tom Krug, Suzanne O'Hara, Mark Watling (Geosyntec Consultants)

Jacqueline Quinn (NASA – Kennedy Space Center, FL)

Nancy Ruiz (NFESC, Port Hueneme, CA)

Chunming Su and Robert Puls (USEPA, Ada, OK)



Geosyntec
consultants



May 2009



Report Documentation Page

Form Approved
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

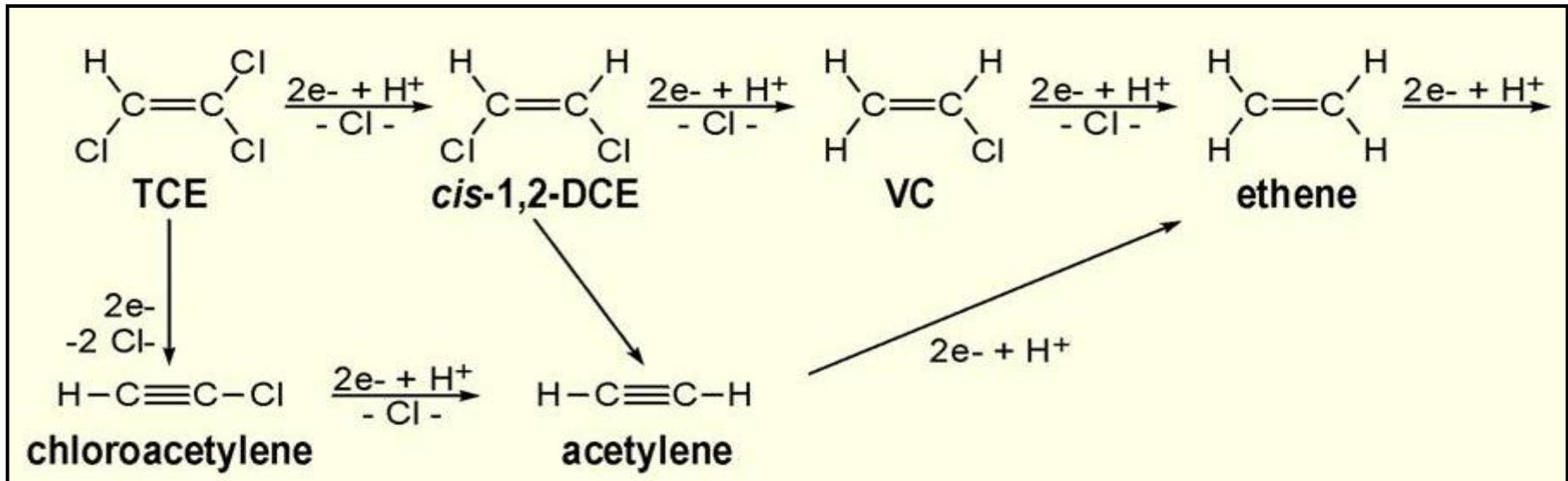
1. REPORT DATE MAY 2009		2. REPORT TYPE		3. DATES COVERED 00-00-2009 to 00-00-2009	
4. TITLE AND SUBTITLE Field Evaluation of the Treatment of DNAPL Using Emulsified Zero-Valent Iron (EZVI)				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Facilities Engineering Command, Engineering Service Center, 1100 23rd Ave, Port Hueneme, CA, 93043				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES Presented at the NDIA Environment, Energy Security & Sustainability (E2S2) Symposium & Exhibition held 4-7 May 2009 in Denver, CO. U.S. Government or Federal Rights License					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 30	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

Outline

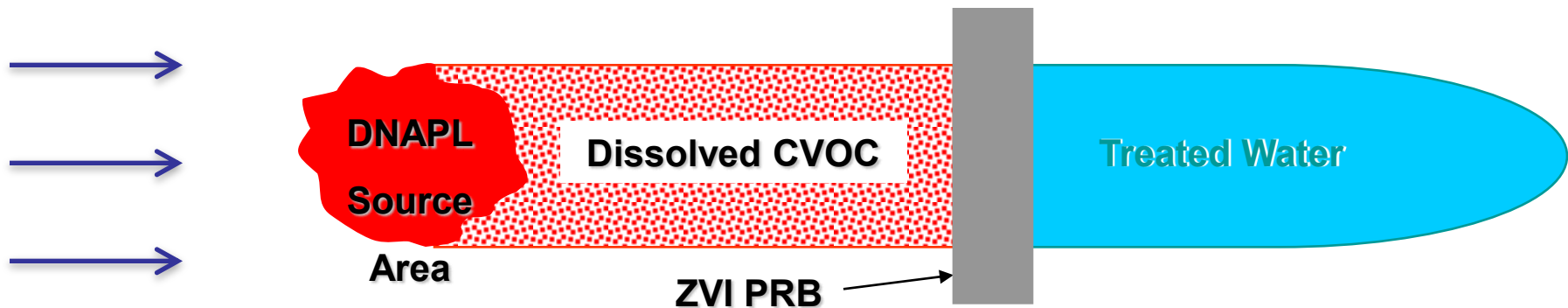
- EZVI Technology Background
- EZVI Applications
- ESTCP Project Objectives
- Overview of Lab Study
- Field Demonstration – Parris Island

ZVI Chemistry

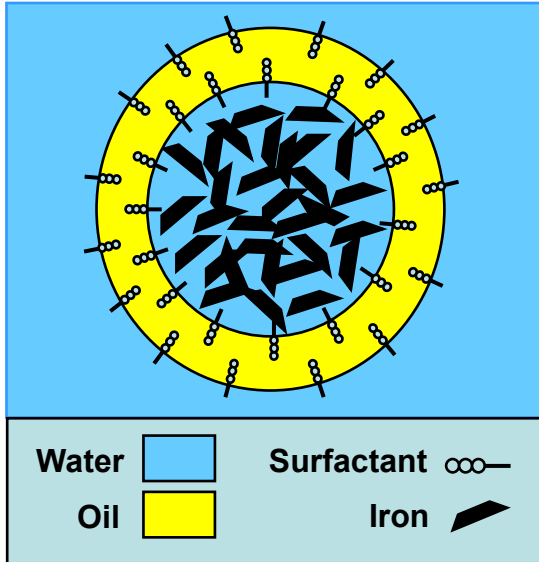
- ZVI is a strong reducing agent
- ZVI is an accepted technology for degradation of dissolved CVOCs such as PCE and TCE
- Basic chemistry the same for granular, micro- or nano-scale ZVI (mZVI or nZVI)



- ZVI Permeable Reactive Barriers (PRBs) with granular iron are effective in treating dissolved CVOCs but:
 - are dependent on dissolution and transport of CVOCs
 - 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



Properties of EZVI



- Emulsion droplets contain iron particles in water surrounded by an oil-liquid membrane
- Oil layer of emulsion is miscible with the DNAPL
- CVOCs diffuse through the oil membrane and are degraded by the ZVI
- EZVI enhances contact between the DNAPL and the ZVI particles
- Vegetable oil act as electron donor and promotes anaerobic biodegradation

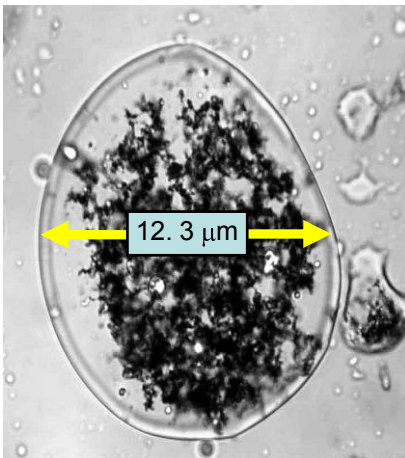
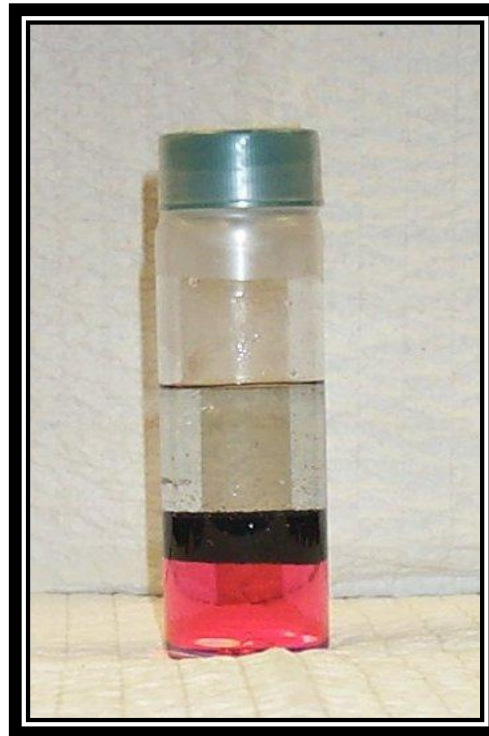


Image of EZVI and DNAPL Contact



**DNAPL
dyed red**



**DNAPL
with nano-scale ZVI**



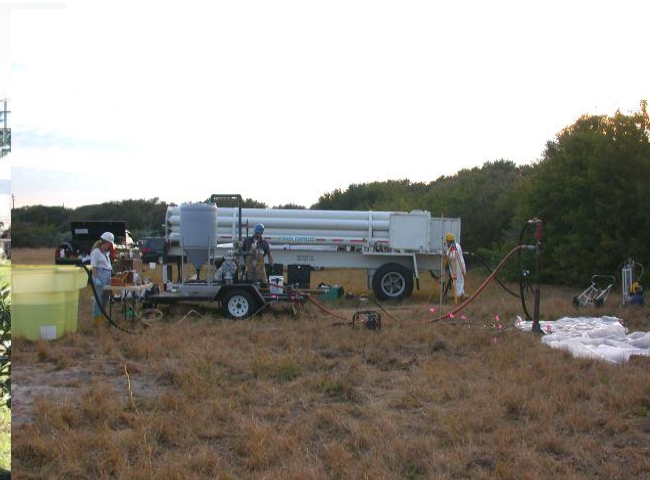
**DNAPL
with EZVI**

EZVI Technical Capabilities

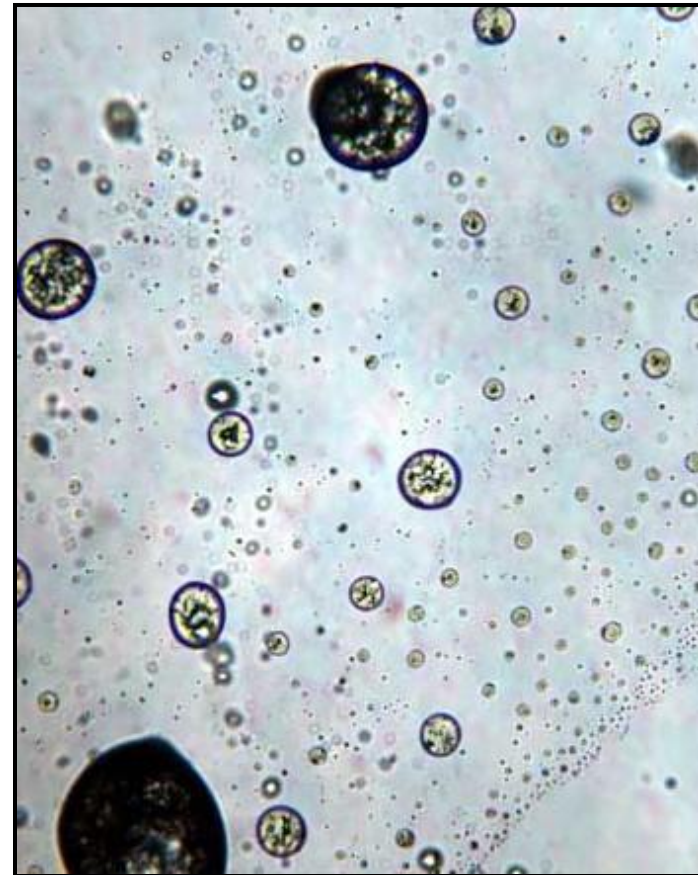
- Combines capabilities of three remediation technologies:
 - Zero-valent iron (ZVI) – abiotic degradation
 - Biodegradation - biodegradation
 - Oil sequestration – mobility reduction
- Enhances contact between ZVI and DNAPL

EZVI Application Methods

- Injection
 - Direct injection
 - Pneumatic injection
 - Pressure pulse injection
 - Hydraulic fracturing
- Large diameter auger mixing
- Viscous fluid can be difficult to emplace in the target treatment interval



- NASA holds the patent for EZVI
- Technology has been successfully commercialized by NASA and has been licensed to six 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
- 16 Sites from 2002 - 2008



ESTCP Project Objectives

- **Laboratory Study:**

- Evaluate degradation mechanisms - Completed 2005

- **Field Demonstration Testing:**

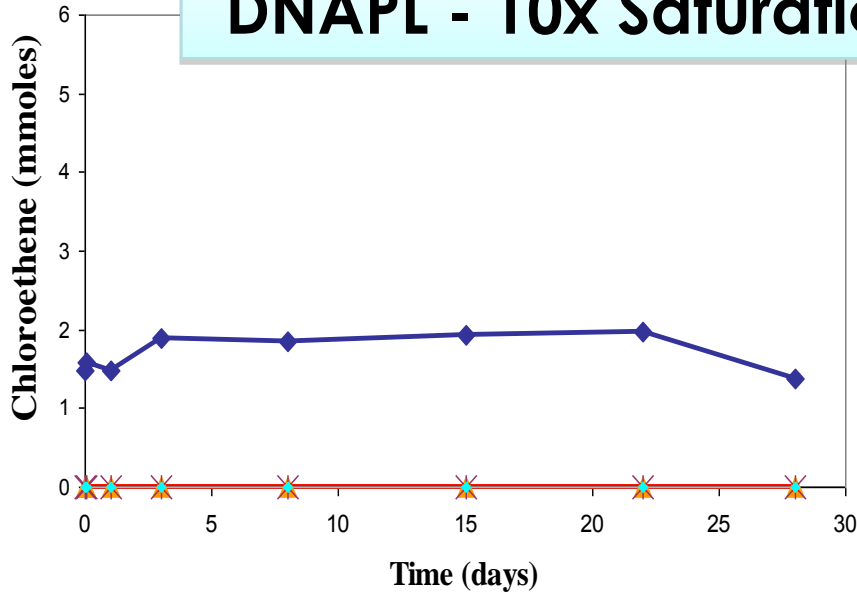
- Inject EZVI into two pilot test areas within a DNAPL source zone using: Direct Injection, Pneumatic Injection
- Evaluate ability of EZVI to reduce mass flux of CVOCs from a DNAPL source zone and reduce the DNAPL mass

Treatability Testing

- Lab tests conducted to evaluate treatment of near saturation dissolved phase concentrations (1000 ppm) and DNAPL (10 x saturation) using:
 - Controls (active and sterile)
 - Vegetable oil & surfactant (Emulsion)
 - nZVI
 - nZVI in EZVI
- Monitor VOCs, DHG and chloride in the water phase of each reactor



DNAPL - 10x Saturation (16.7 mmoles)



◆ TCE ▲ cis-1,2-DCE ✱ VC — Ethene — Ethane

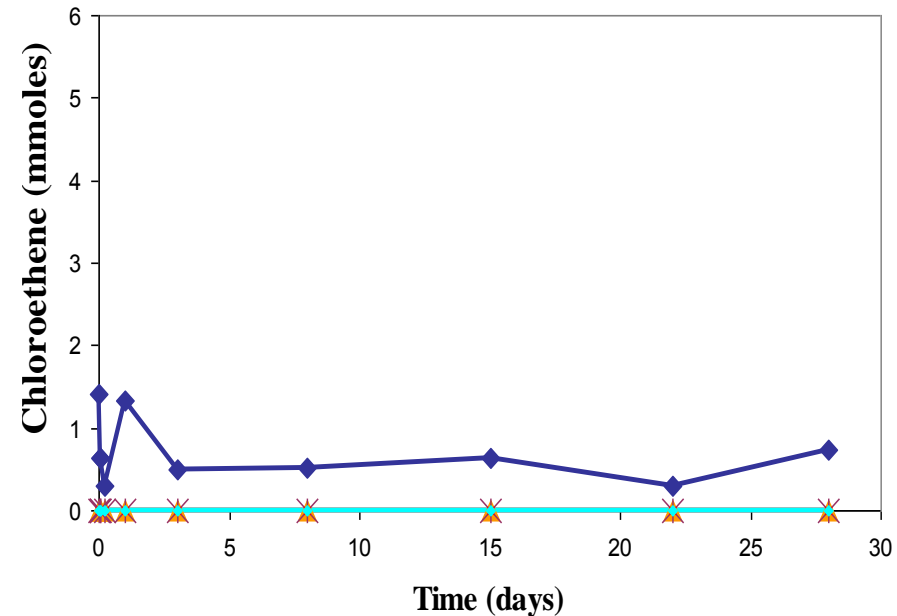
Active Control

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



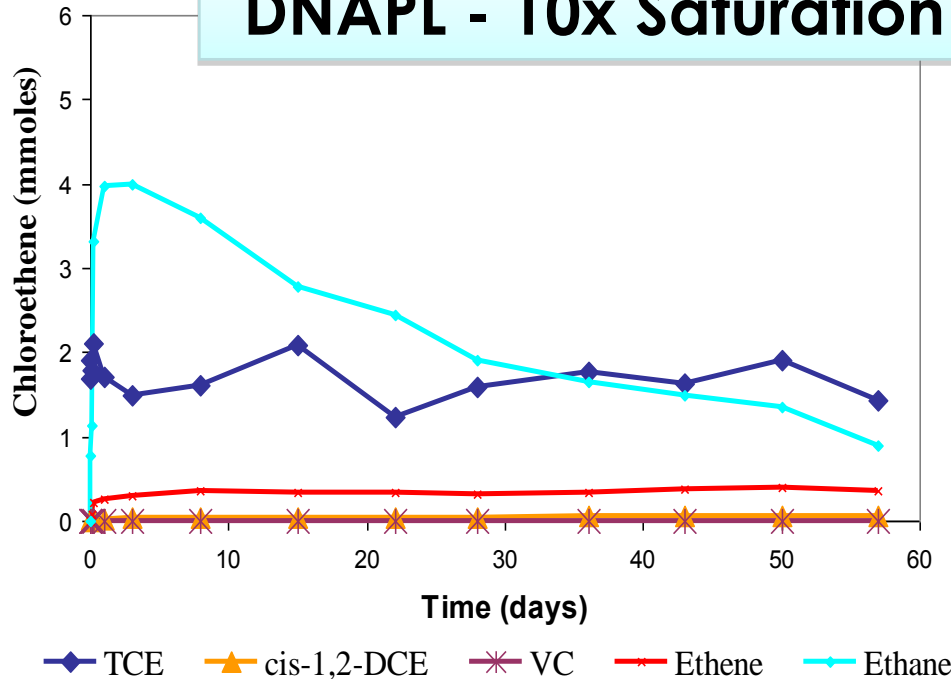
Oil Emulsion Treatment

- 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



◆ TCE ▲ cis-1,2-DCE ✱ VC — Ethene — Ethane

DNAPL - 10x Saturation (16.7 mmoles)

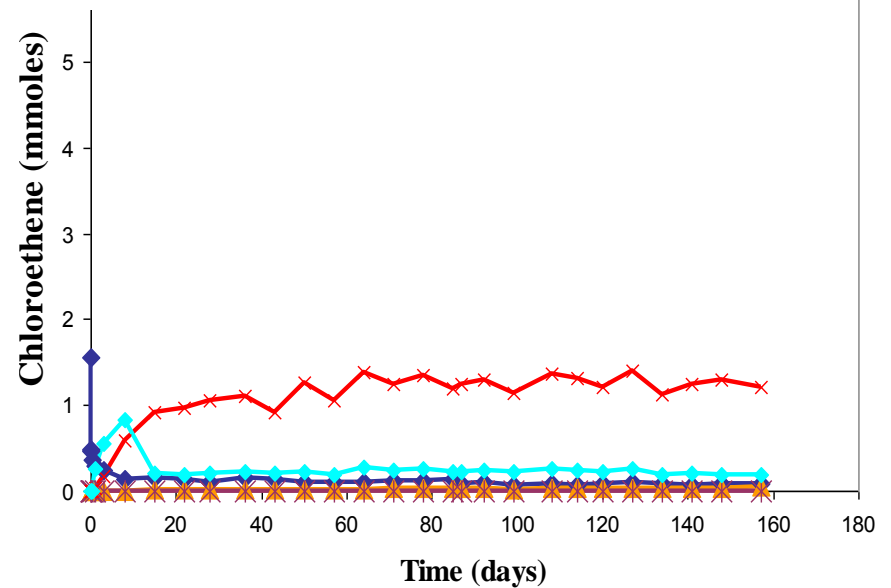


VI Treatment

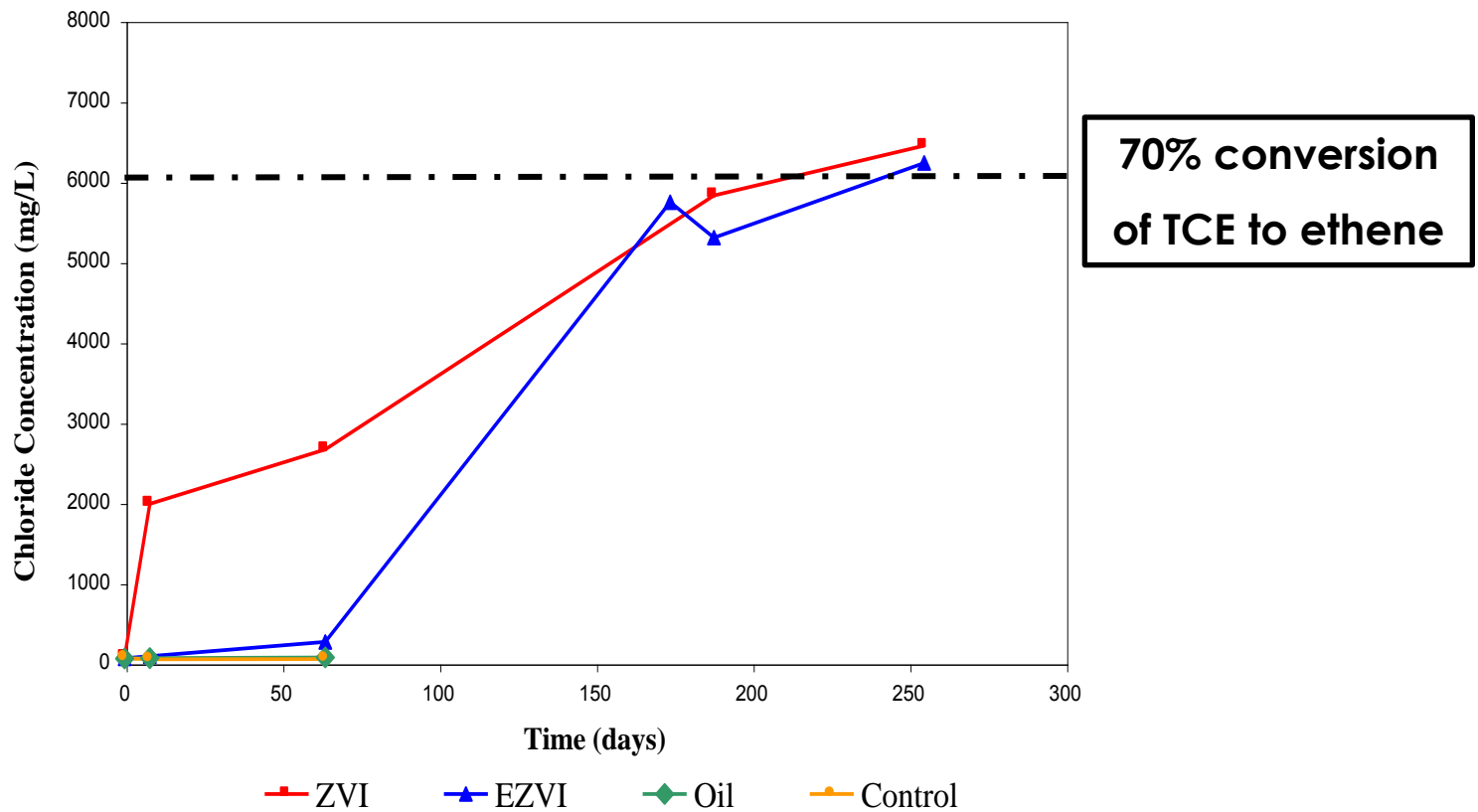
stable at saturation concentration
degradation by-products observed (ethane and ethene)
chloride production indicates degradation of ~73% of TCE

EZVI Treatment

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



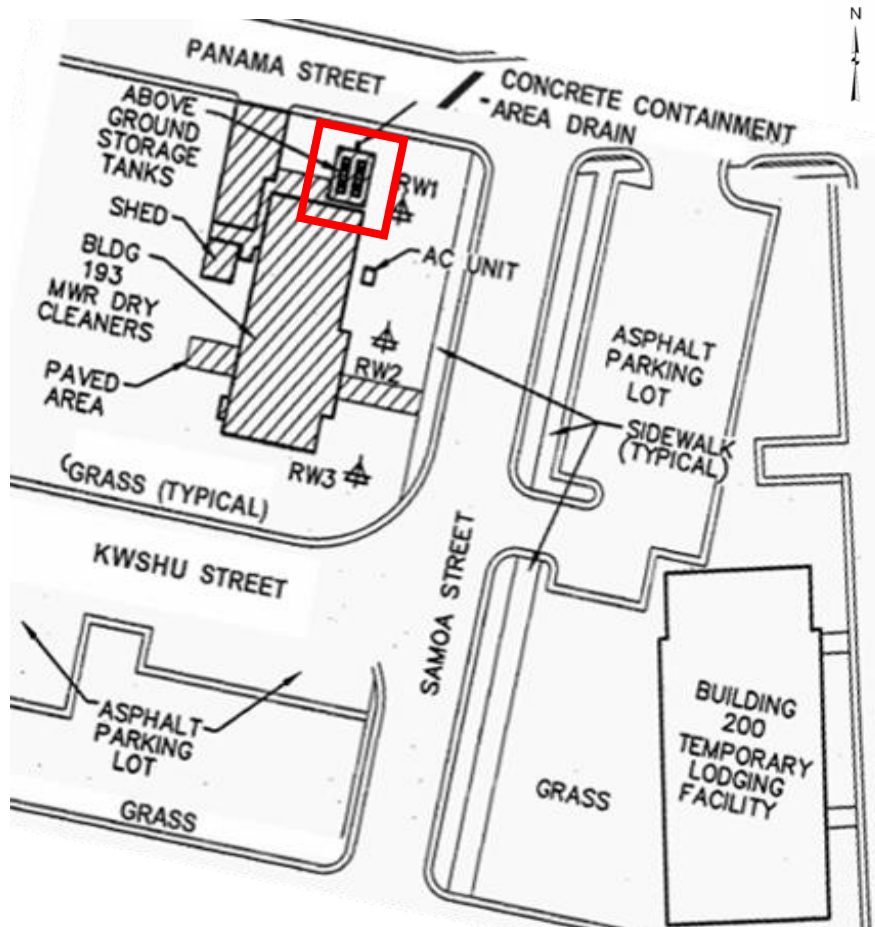
EZVI Lab Testing – Chloride Production



Conclusions – Lab Testing

- 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
- Impacts of biodegradation not significant in these tests which utilized synthetic groundwater and no soil (expect to see biodegradation with emulsion and EZVI)

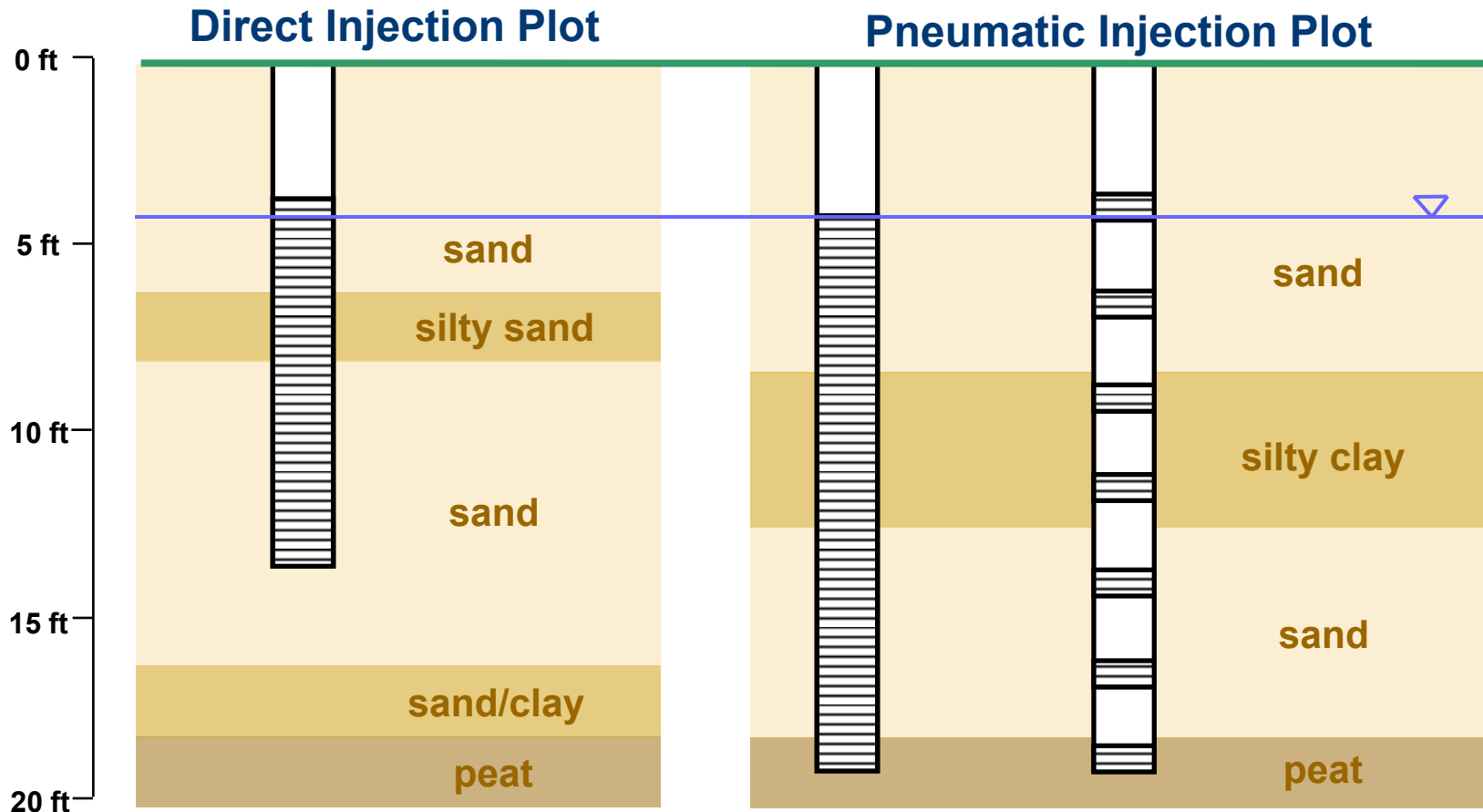
Case Study - Parris Island



- 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 above and below ground storage tanks

Demonstration Site

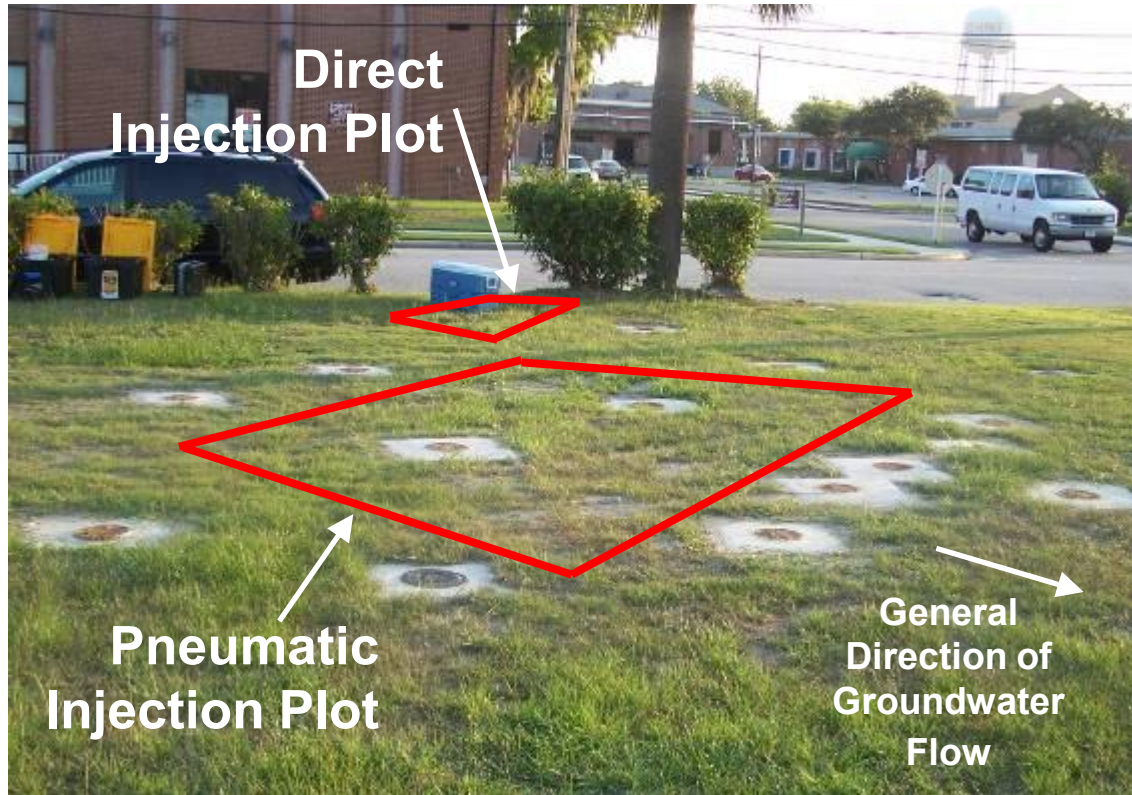
Fully screened and multilevel wells



Demonstration Site



Multilevel Well Construction



Direct and Pneumatic Injection Plots

EZVI Preparation

- EZVI prepared on-site by mixing nano-scale iron (Toda), corn oil, surfactant and water in drums using top mounted industrial mixer
- EZVI pumped from mixing drums into injection tanks



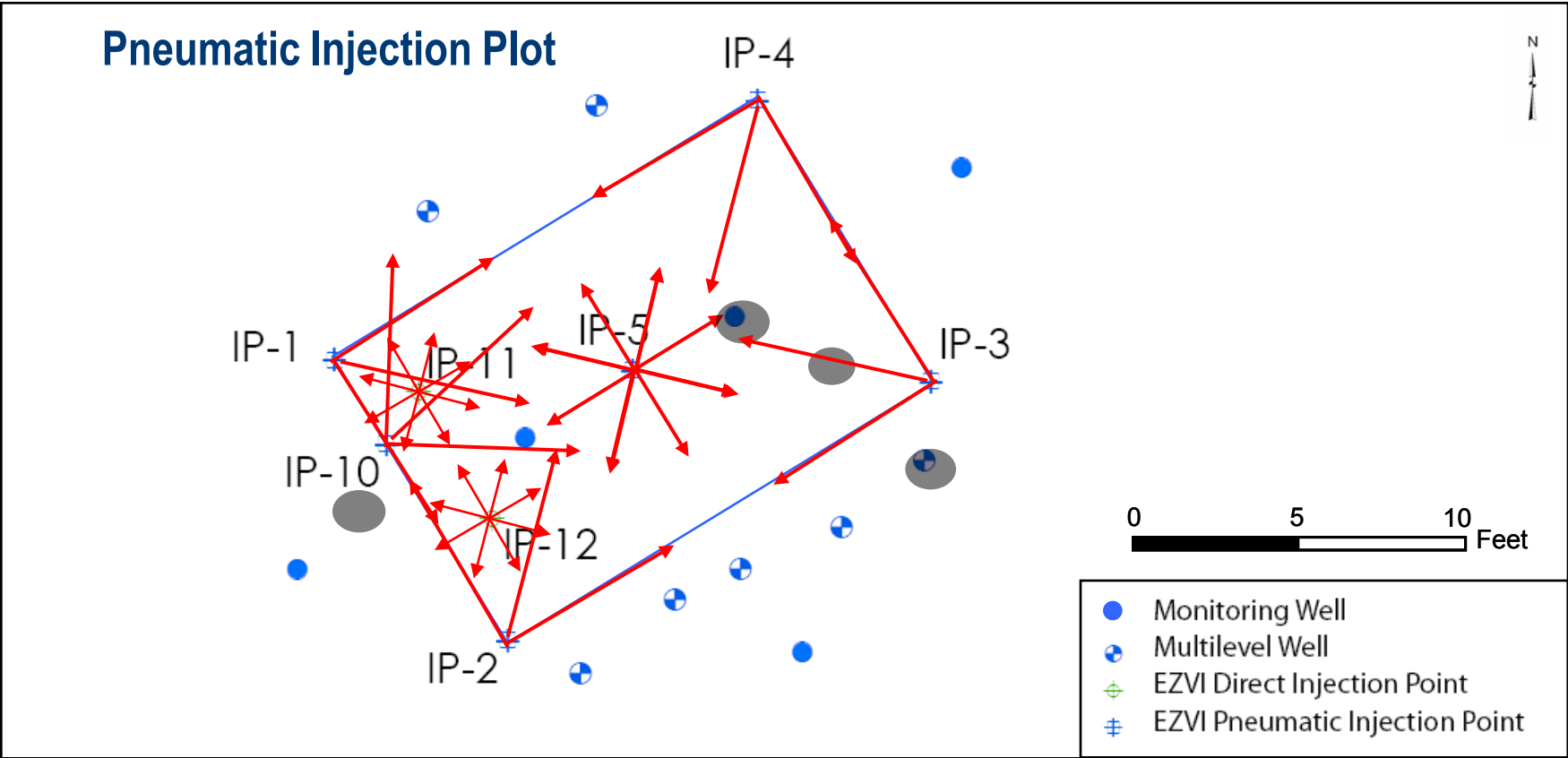
EZVI Injections

Pneumatic Injection Plot

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



Pneumatic Injection Plot



EZVI Injections

- EZVI daylighted in both Pneumatic and Direct Injection test plots

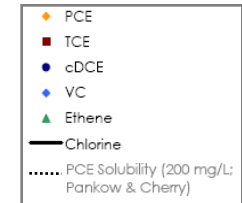
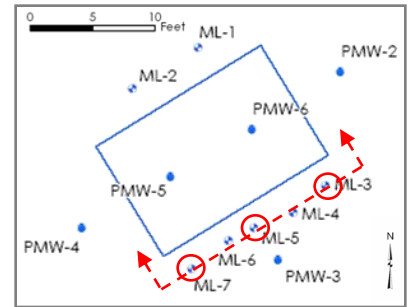
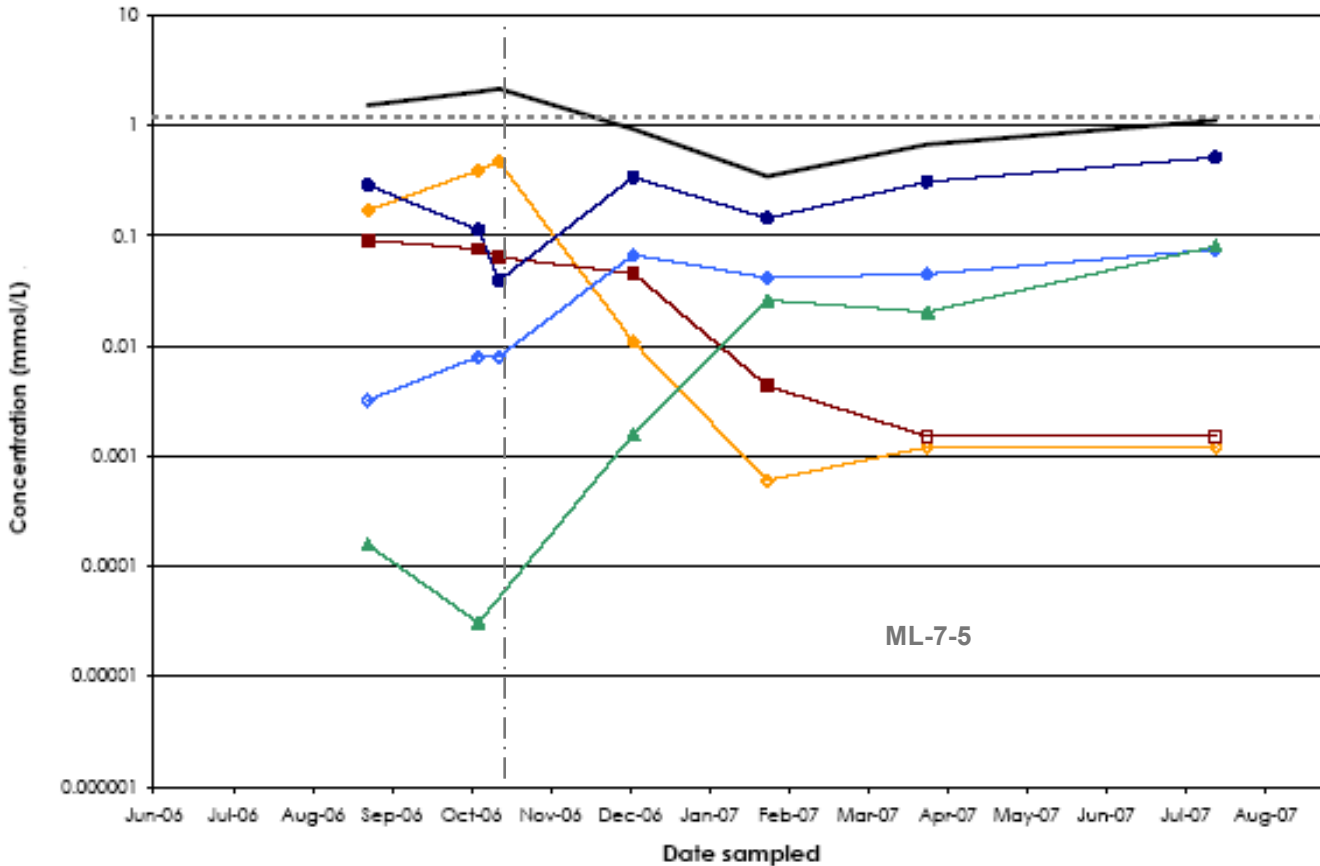
Pneumatic Injection plot (daylighting around ML-3 pad, downgradient of plot)



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

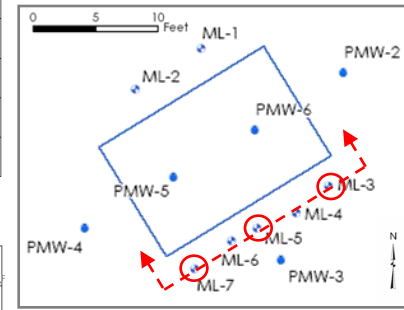
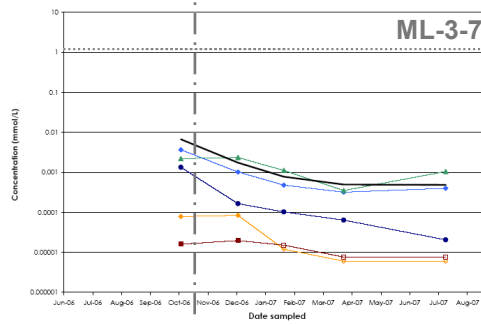
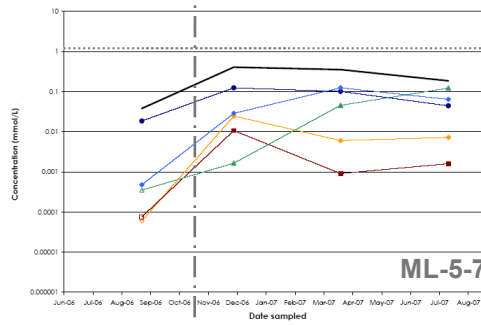
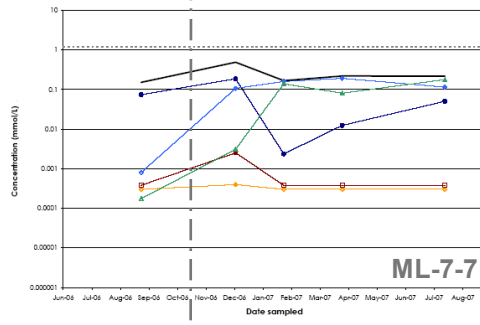
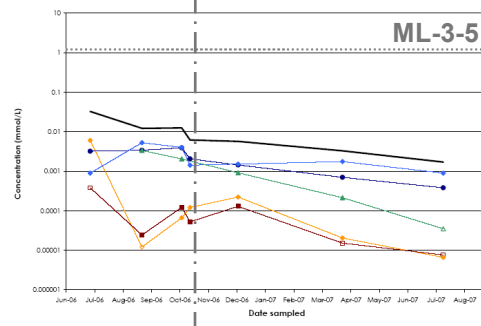
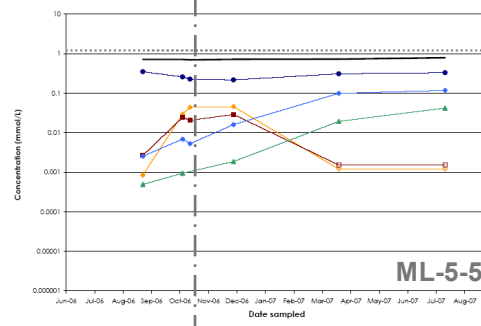
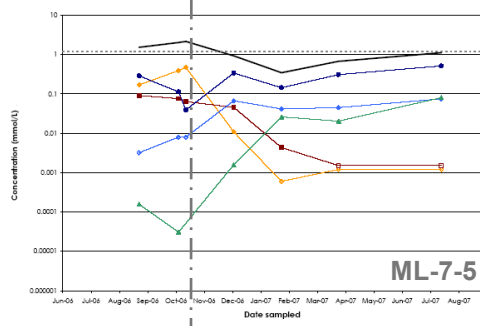
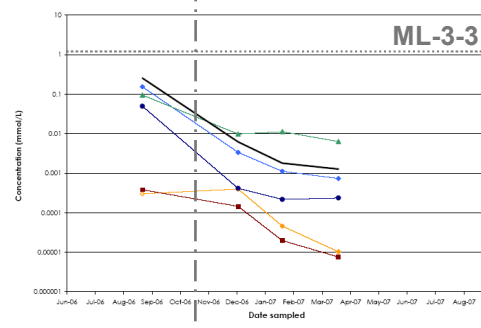
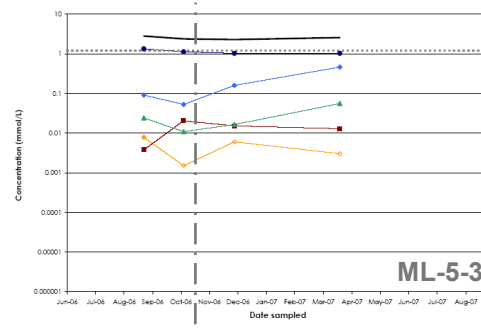
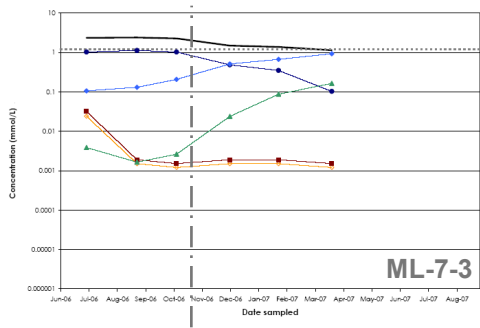


VOC Trends: Downgradient Well



| EZVI
 | Injections
 |

VOC Trends: Downgradient wells in Pneumatic Injection Plot



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

— EZVI
Injections

Summary of Case Study

- 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 distributing EZVI due to shallow application and short-circuiting up existing investigation boreholes

Modified EZVI Applications

- mZVI versus nZVI to make EZVI
- Co-injection of ZVI and vegetable oil
- Bioaugmentation to enhance biodegradation
- Applications for co-mingled plumes or sources where either ZVI or bioremediation on its own wouldn't work

Acknowledgements

- Project funding provided by ESTCP (ER-0431)
- USEPA (GWERD, National Risk Management Research Laboratory) provided drill rig for soil cores and well installations. Also providing field sampling support, equipment and analytical support
- Pneumatic injections performed by Pneumatic Fracturing, Inc. (Alpha, NJ)
- Direct injections performed by Vironex, Inc. (Golden, CO)
- Tim Harrington, Parris Island MCRD

Supplemental Slides

Cost of EZVI

- Cost of nZVI and to lesser extent mZVI drives cost of EZVI
- Cost of other ingredients are minimal (up to \$6/gal)
- Small volumes can be prepared on-site; larger volumes prepared and shipped to the site
- Costs for EZVI with nZVI significantly more than with mZVI:
 - ~\$10/gallon with BASF mZVI
 - ~\$28/gallon with Toda nZVI

Iron Product	Supplier	Cost
Nano-scale ZVI	Toda America	\$26-\$34 / lb
Micro-scale ZVI (40,000 nm)	Hepure (ARS)	\$1.00 to \$1.70/lb
Micro-scale ZVI (up to 3,000 nm)	BASF	\$4.00 / lb
Granular Iron (comparison only, can't use to make EZVI)	Peerless Metal Products, Master Builders, QMP, Connelly	\$0.40 / lb