EMULSIFIED ZERO-VALENT IRON
Laboratory and Field Testing

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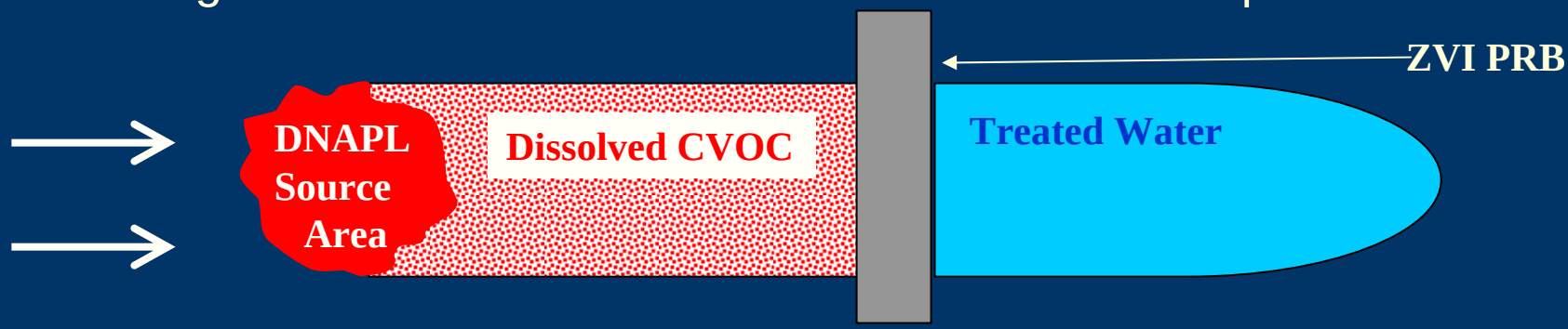
Research Participants

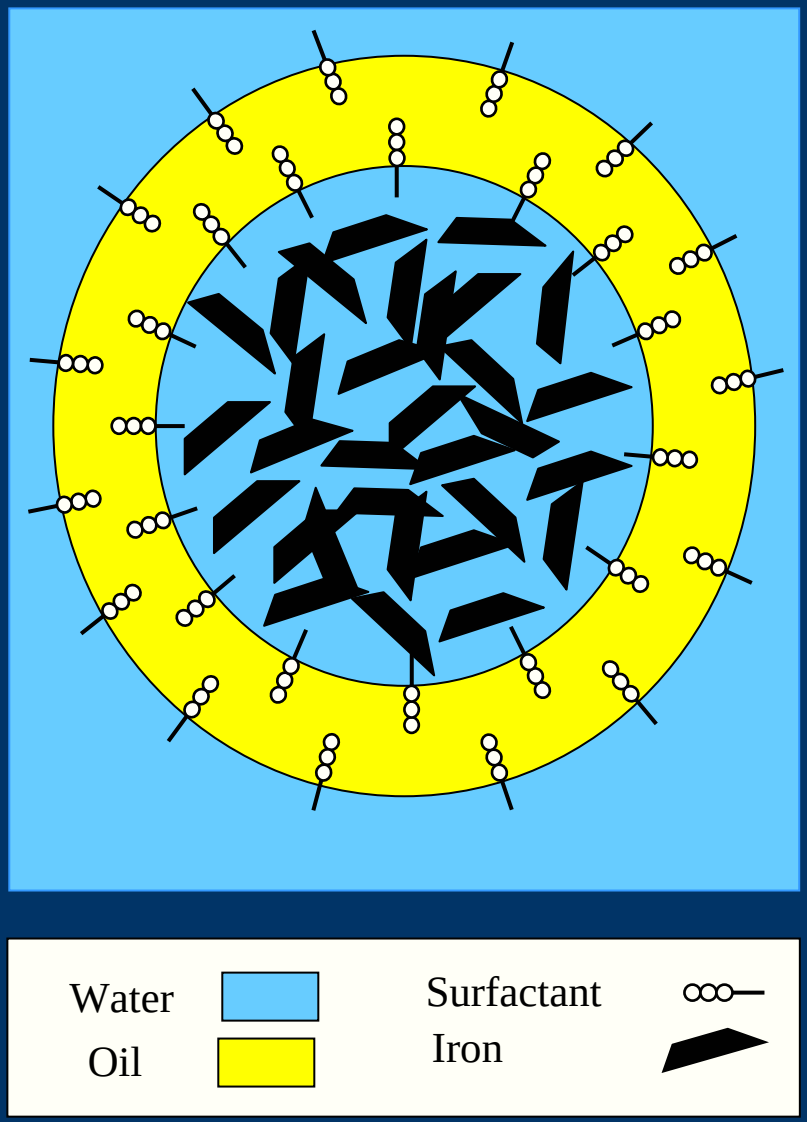
- Chris Clausen and Cherie Geiger from University of Central Florida
- Suzanne O'Hara, Tom Krug and Dave Major from GeoSyntec
- Tom Holdsworth from USEPA NRMRL
- Bob Puls and Chunming Su from USEPA GWERD
- Nancy Ruiz from NFESC Navy

Technology Rationale

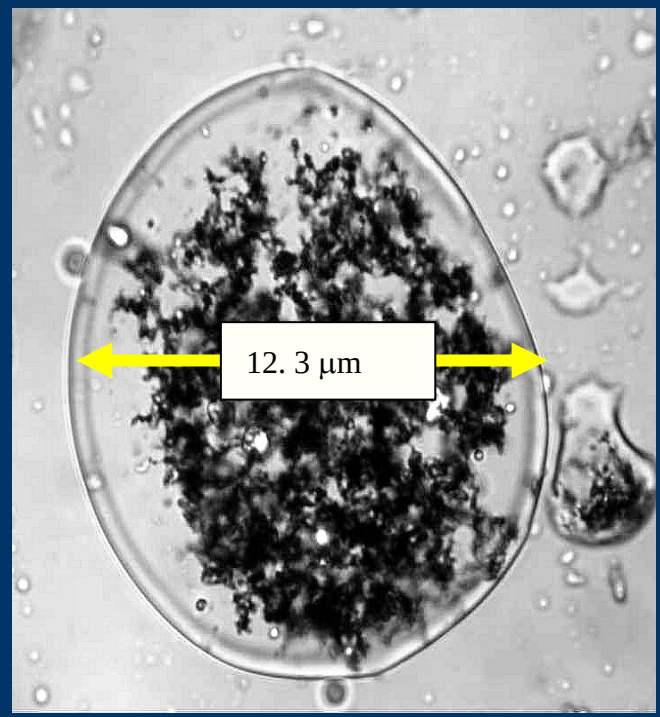
- **ZVI PRBs are effective in treating dissolved CVOCs but:**
  - are dependent on dissolution and transport of CVOCs; and
  - do little to reduce the clean up time and long-term monitoring costs.
- ZVI needs to be in the presence of water to promote reductive dehalogenation → injection of ZVI into a DNAPL source zone will only treat the dissolved phase at the edges of the DNAPL.
- EZVI can be used to enhance degradation of DNAPLs by enhancing contact between the DNAPL and the ZVI particles.



Properties of EZVI



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



EZVI In Contact with DNAPL

DNAPL
dyed red

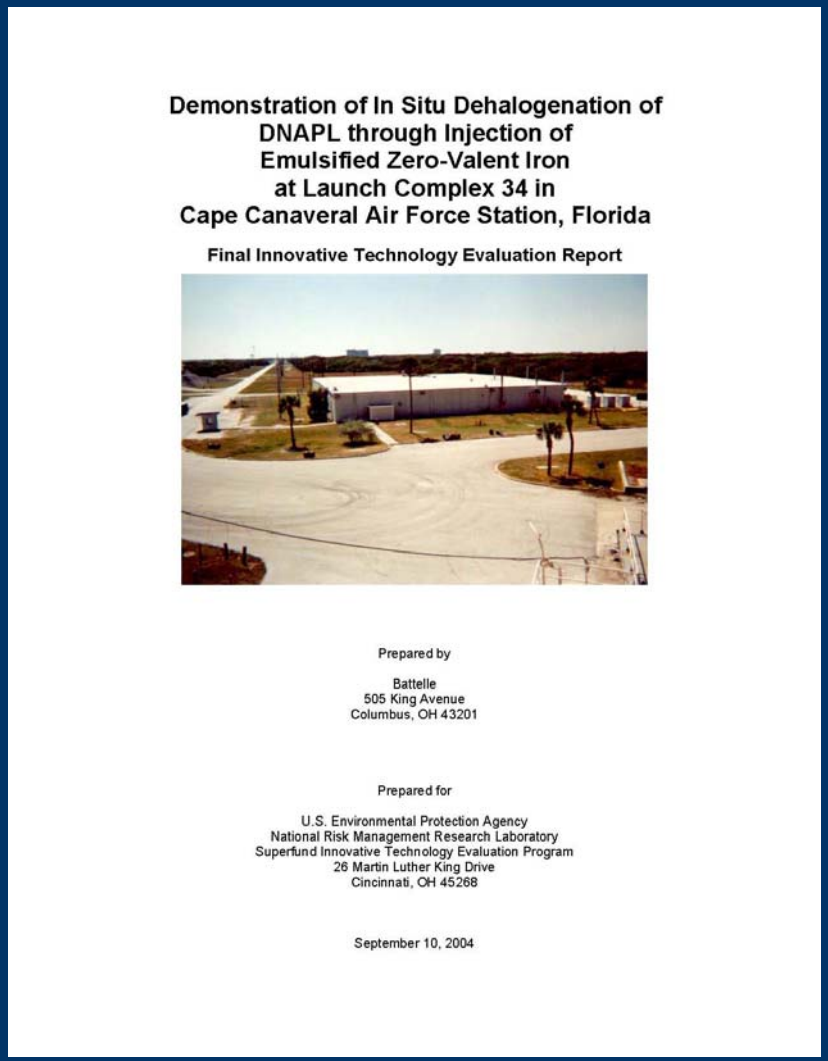
DNAPL with
micro-scale ZVI

DNAPL
with EZVI

EZVI Technology Evaluation
Demonstration at LC34

- Demonstration conducted at NASA's LC34.
- Performance evaluation based on GW mass flux and TCE mass in pre- and post-treatment soil cores
- Monitored changes in CVOCs in:
  - GW (5 depth intervals, 2 upgradient and 2 downgradient wells); and
  - soil cores (8 depth intervals, 6 locations)
- EPA SITE Program independently evaluated technology demonstration

Field Demo EPA SITE Program Report



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

- Battelle conducted an independent evaluation of the EZVI demonstration at LC34

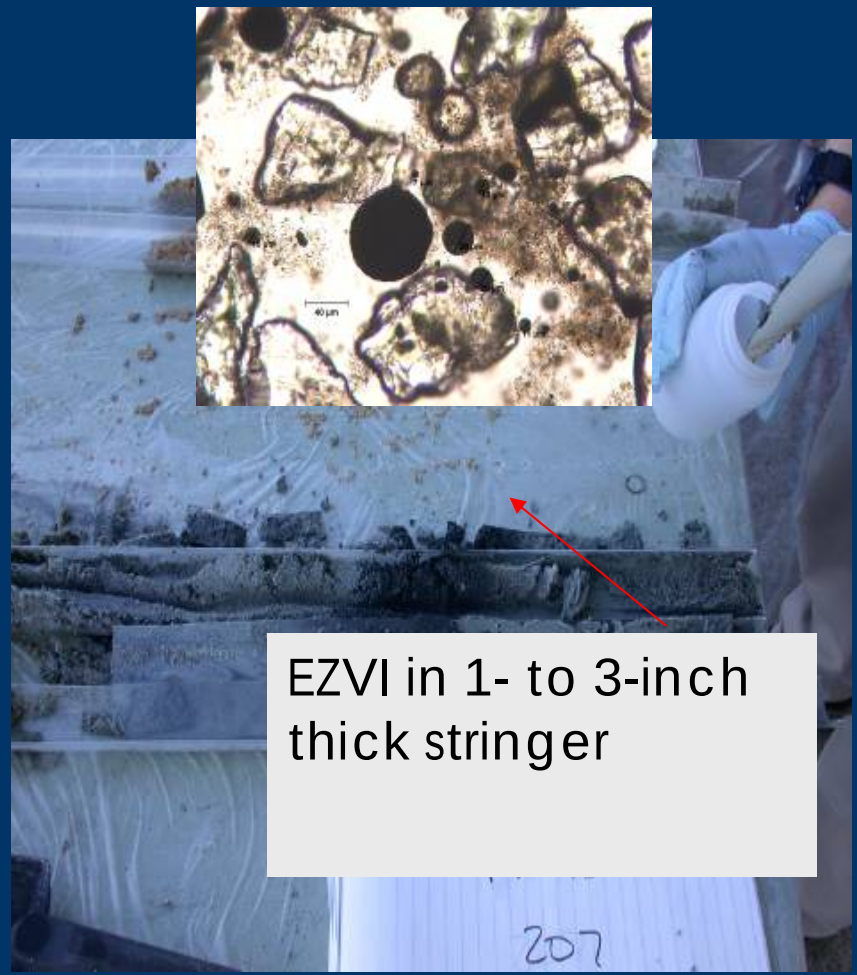
Field Demo Paper in ES&T

- 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.

Results of Demo at LC34

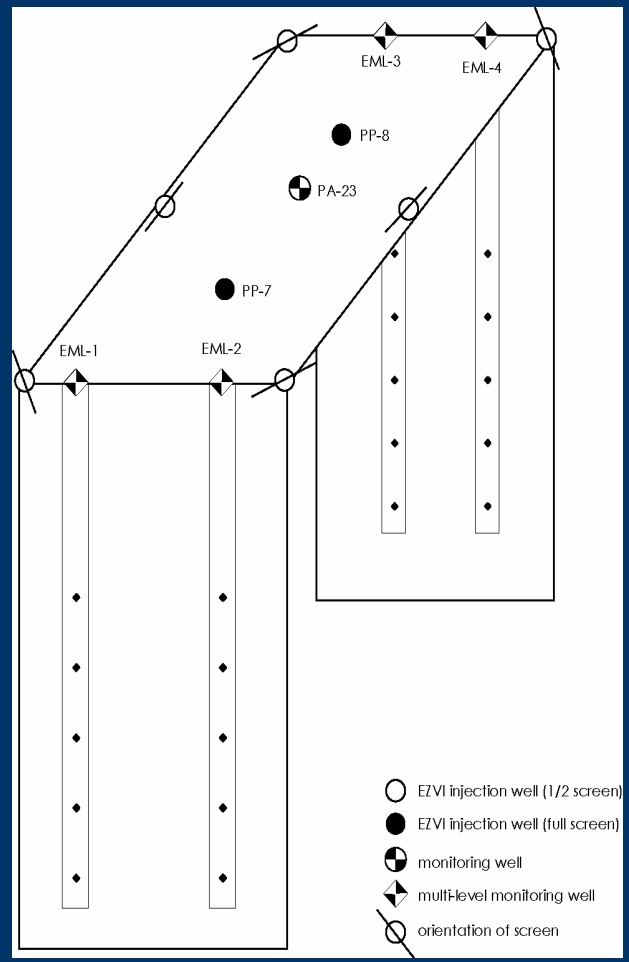
Soil Core Samples:

- Stated objective of 50% removal of total TCE
- EZVI migrated to shallow intervals with PPT injection
- Significant reduction of TCE in four months (>80%) where EZVI was present
- Average reduction of 58%



Results of Demo at LC34

- **<u>Groundwater Samples:</u>**
  - Significant reduction (60 to 100%) of TCE in target depths.
  - Reduction of 56% in the Mass Flux.
  - Elevated cis-1,2-DCE, VC suggest biodegradation due to oil as an electron donor may also be significant



Recommendations From LC34 Demonstration

- Promising results at LC34 but needed to further evaluate:
  - how to control placement of EZVI in subsurface
  - the contribution of the abiotic and biological components of the degradation
- ESTCP funding acquired to address these questions

ESTCP-funded 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)
  - Nano-scale zero-valent iron (nZVI)
  - Emulsified zero-valent iron (EZVI)

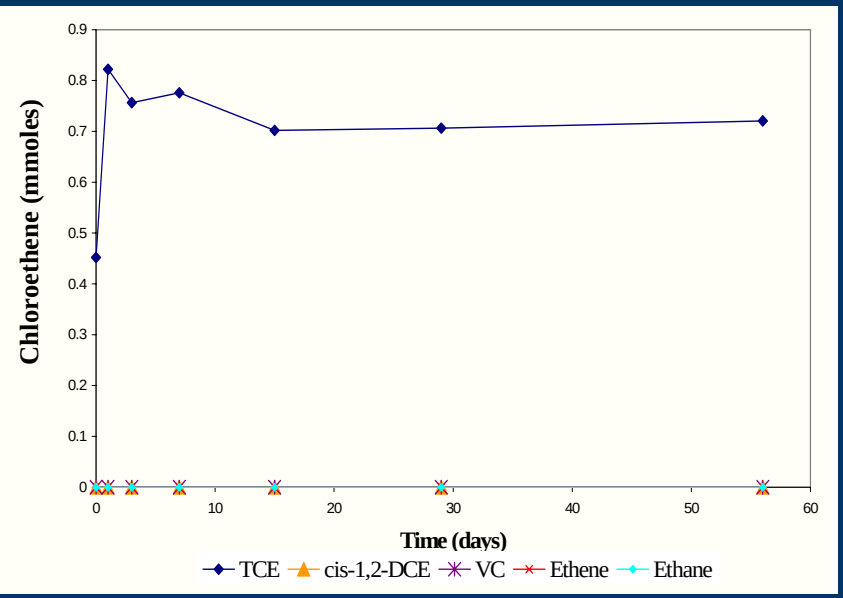
- Monitor VOCs, DHG and Chloride

- Treatability tests done in triplicate and each test set up is done in both sterile and non-sterilized set ups

Dissolved Phase Treatments

- Near saturation concentrations of TCE
- TCE of 1,000 mg/L (0.8 mmoles per bottle)
- nZVI added to achieve 5 times theoretical ZVI requirement to degrade TCE

Dissolved Phase Testing (1)

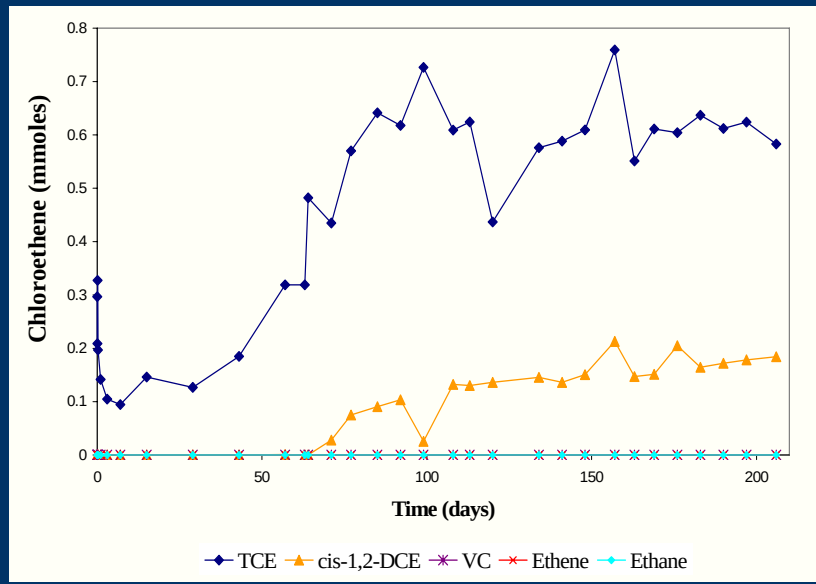


Active Control

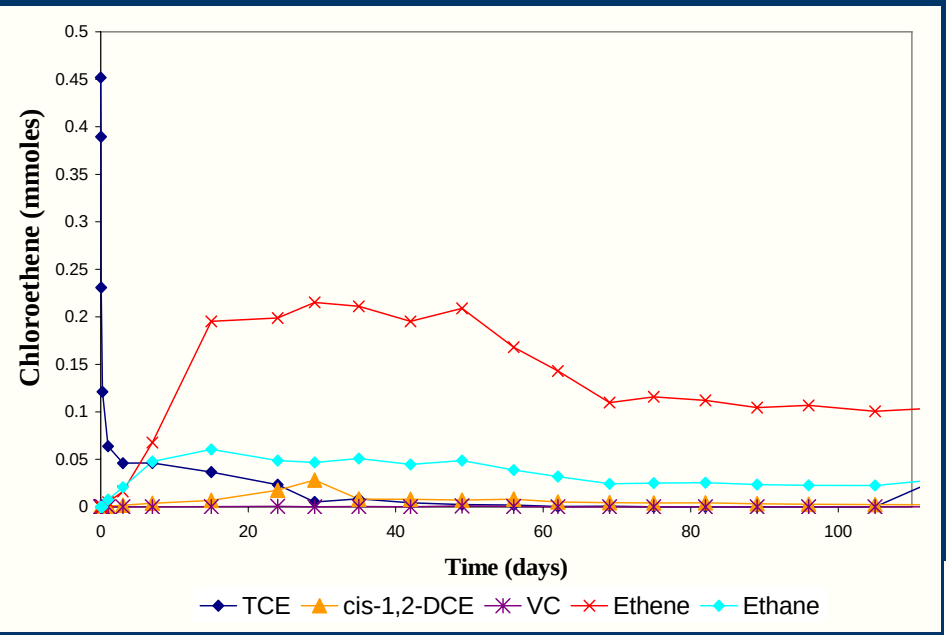
- No losses of TCE or production of degradation byproducts observed in control treatments

Oil Emulsion Treatment

- TCE concentration drops to 0.1 mmols - sequestered in oil
- No degradation by-products observed until ~day 50 when pH buffered and re-bioaugment with KB-1
- Impacts of biodegradation not significant in these tests which utilized DI water and no soil



Dissolved Phase Testing (2)

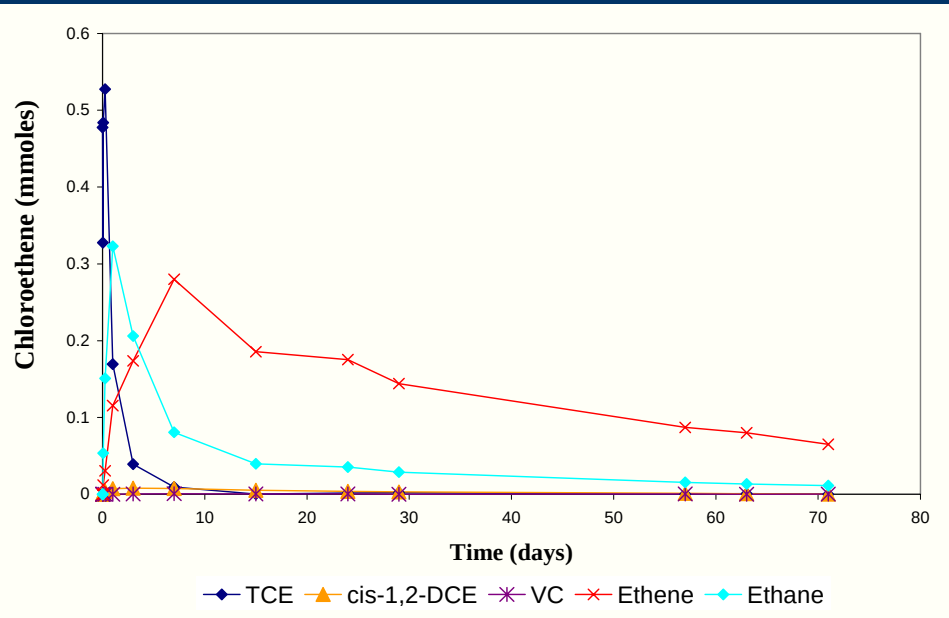


nZVI Treatment

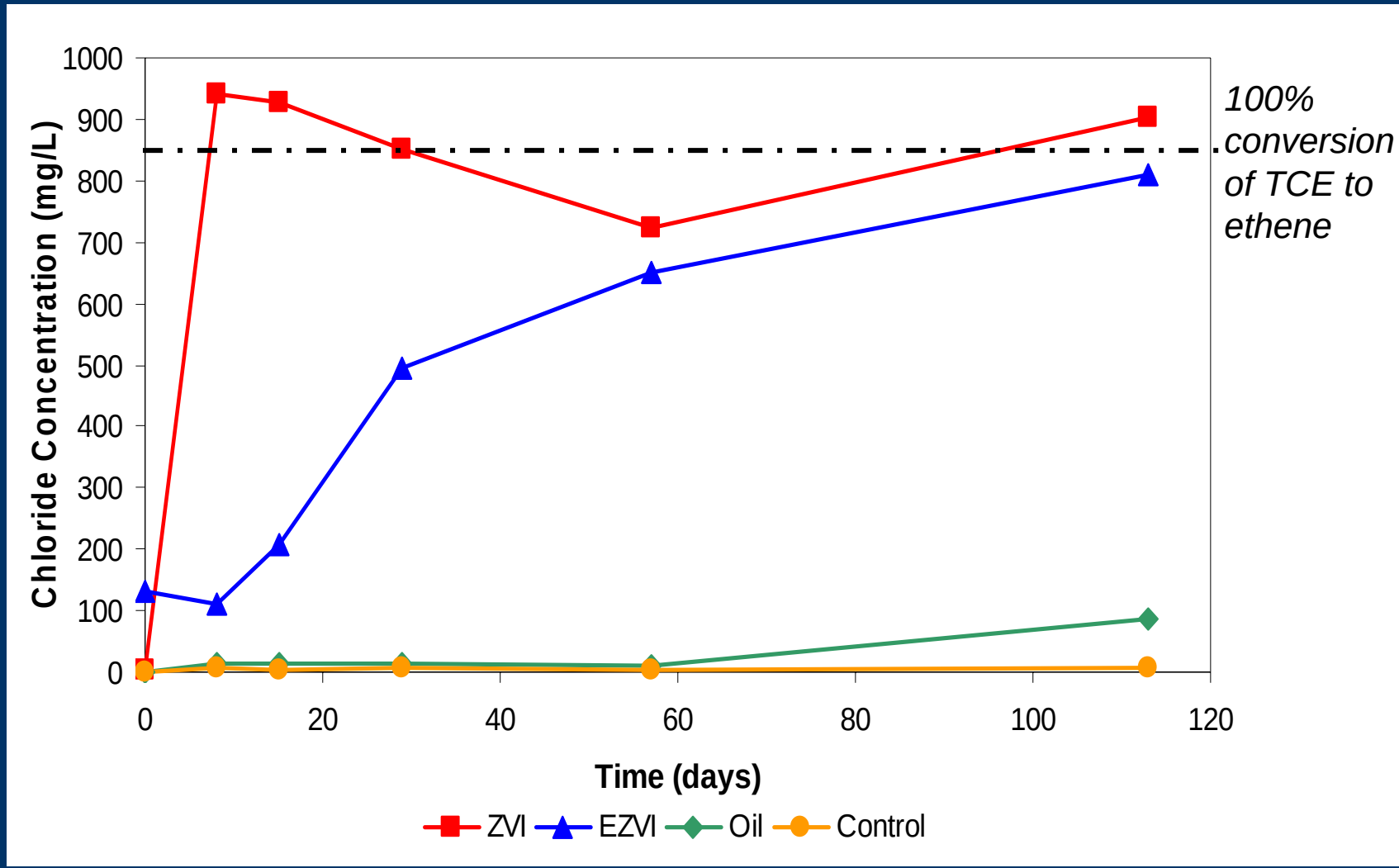
- TCE concentrations drops very rapidly
- Undergoes rapid and complete degradation
- TCE is non-detect by day 71

EZVI Treatment

- TCE concentration drops very rapidly
- EZVI treatment undergoes slightly slower degradation but also complete degradation
- TCE is non-detect by day77



Chloride Production with Dissolved TCE



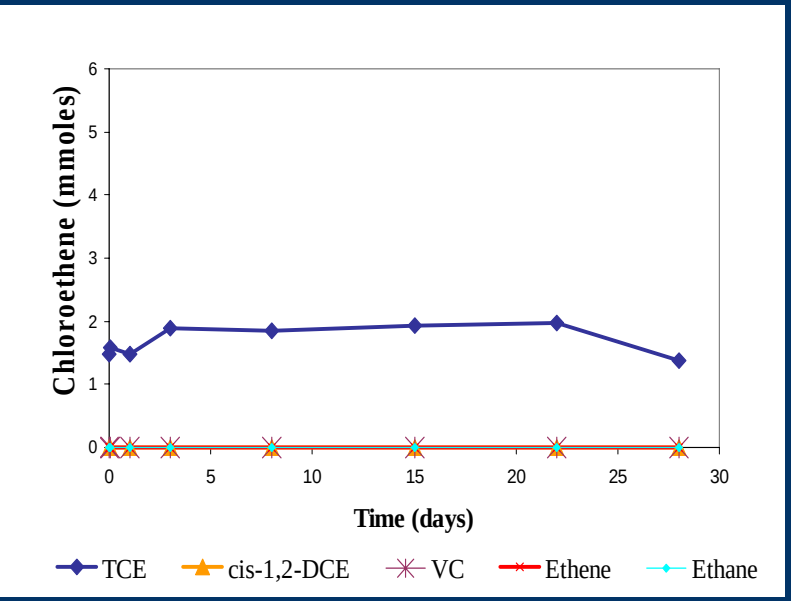
Conclusions - Dissolved Phase Testing

- Dissolved Phase Testing:
  - Lab tests show that EZVI degradation, especially at early times, is mainly due to ZVI (abiotic)
  - Abiotic degradation of the ZVI in the EZVI is not adversely impacted by the oil
- So why use the EZVI if the nZVI promotes rapid and complete degradation?
- In the presence of dissolved phase the ZVI may be slightly faster but in the presence of DNAPL the advantages of the EZVI become apparent

DNAPL Phase Treatments

- 10x saturation concentrations of TCE
- TCE of 10,000 mg/L (16.7 mmoles per bottle)
- nZVI added to achieve 2 times theoretical ZVI requirement to degrade TCE

DNAPL Testing (1)

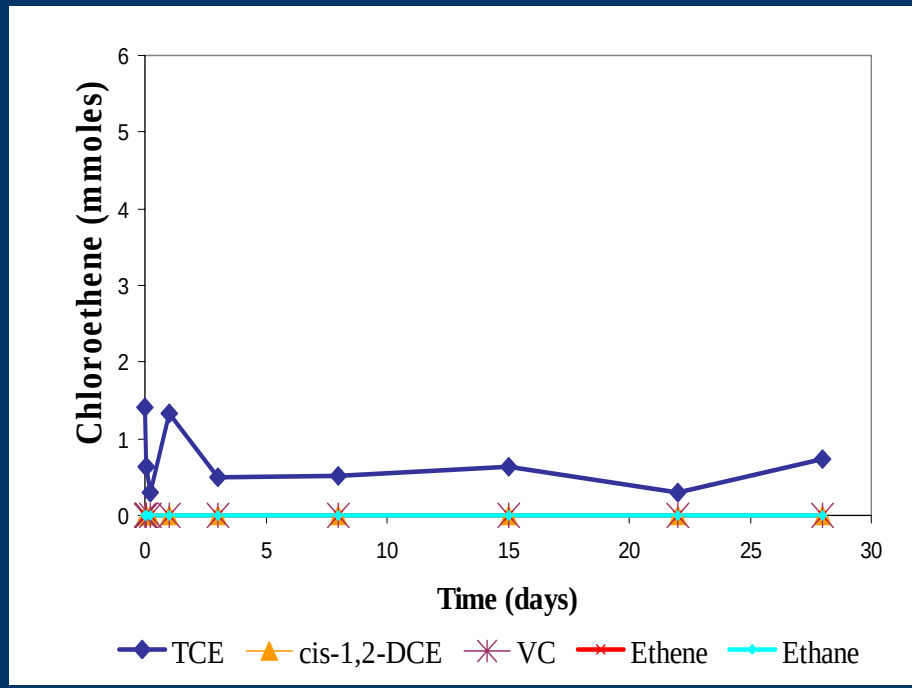


Active Control

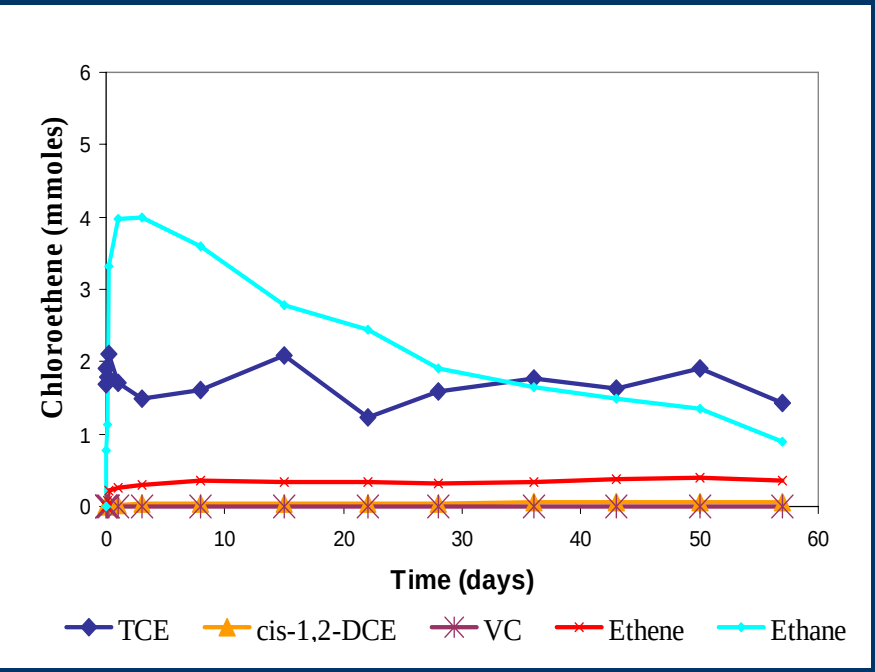
- TCE at saturation concentration
- No degradation by-products observed (no DHG or chloride)

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



DNAPL Testing (2)

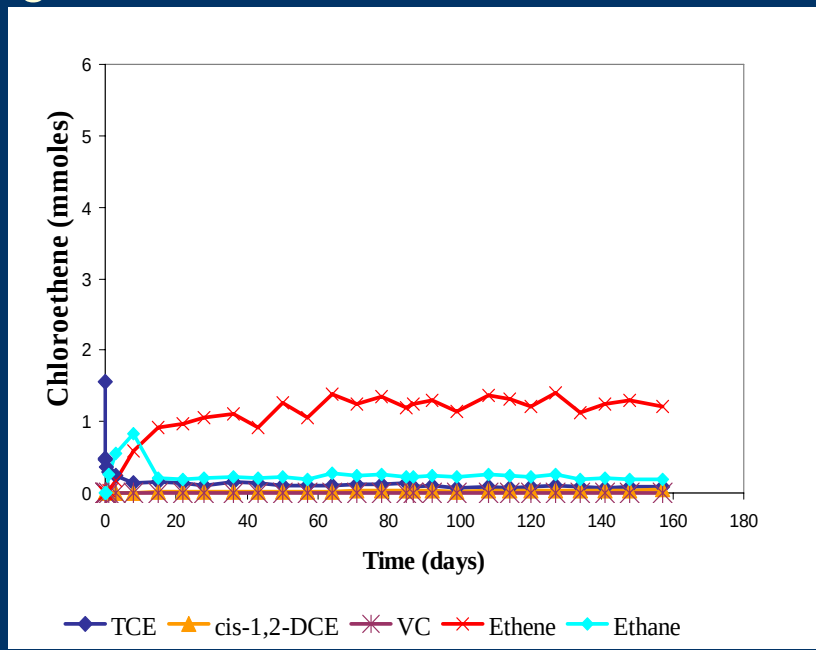


nZVI Treatment

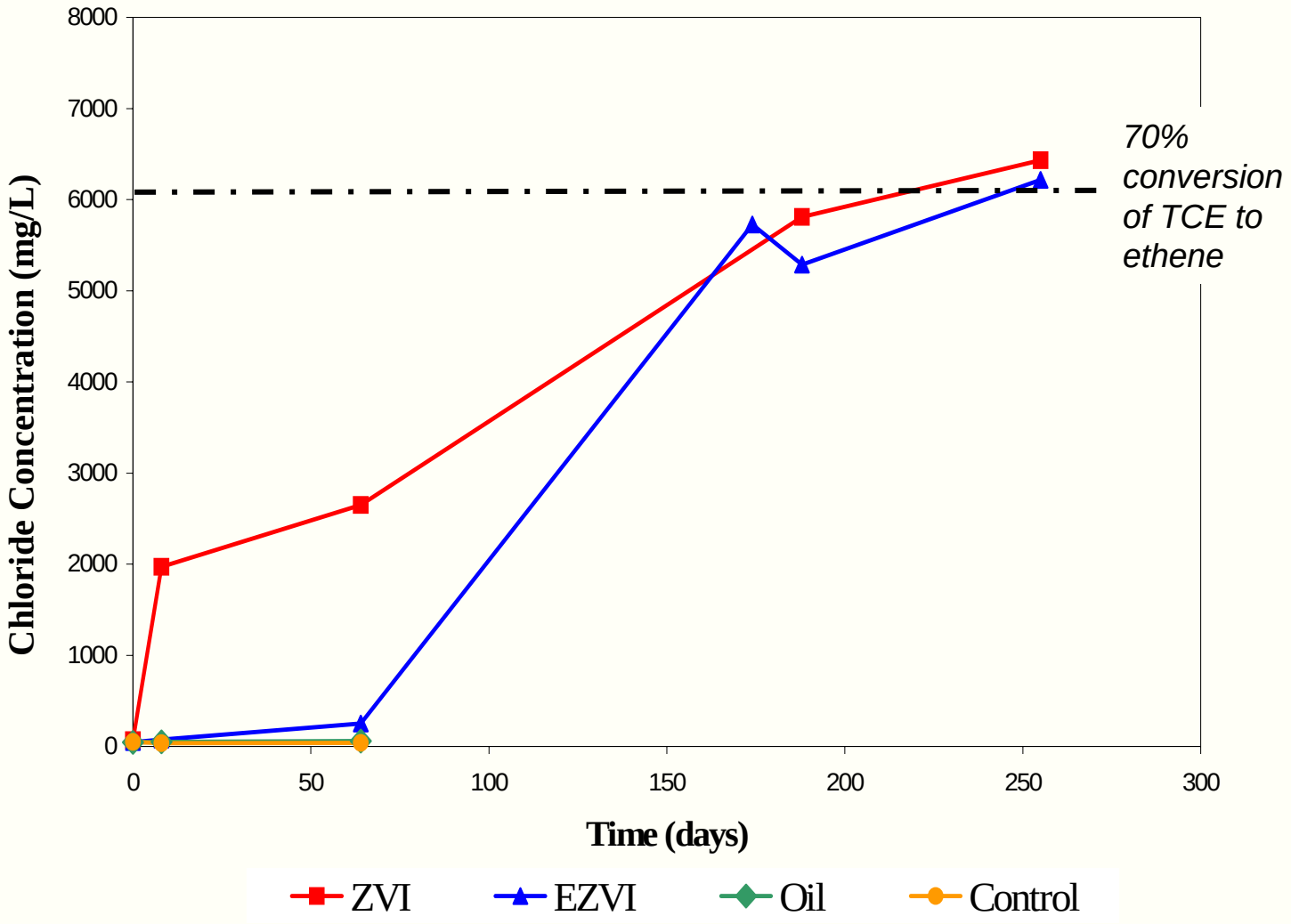
- TCE stable at saturation concentration
- Degradation by-products observed (ethane and ethene)
- Chloride production indicates degradation of ~73% of TCE

EZVI Treatment

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



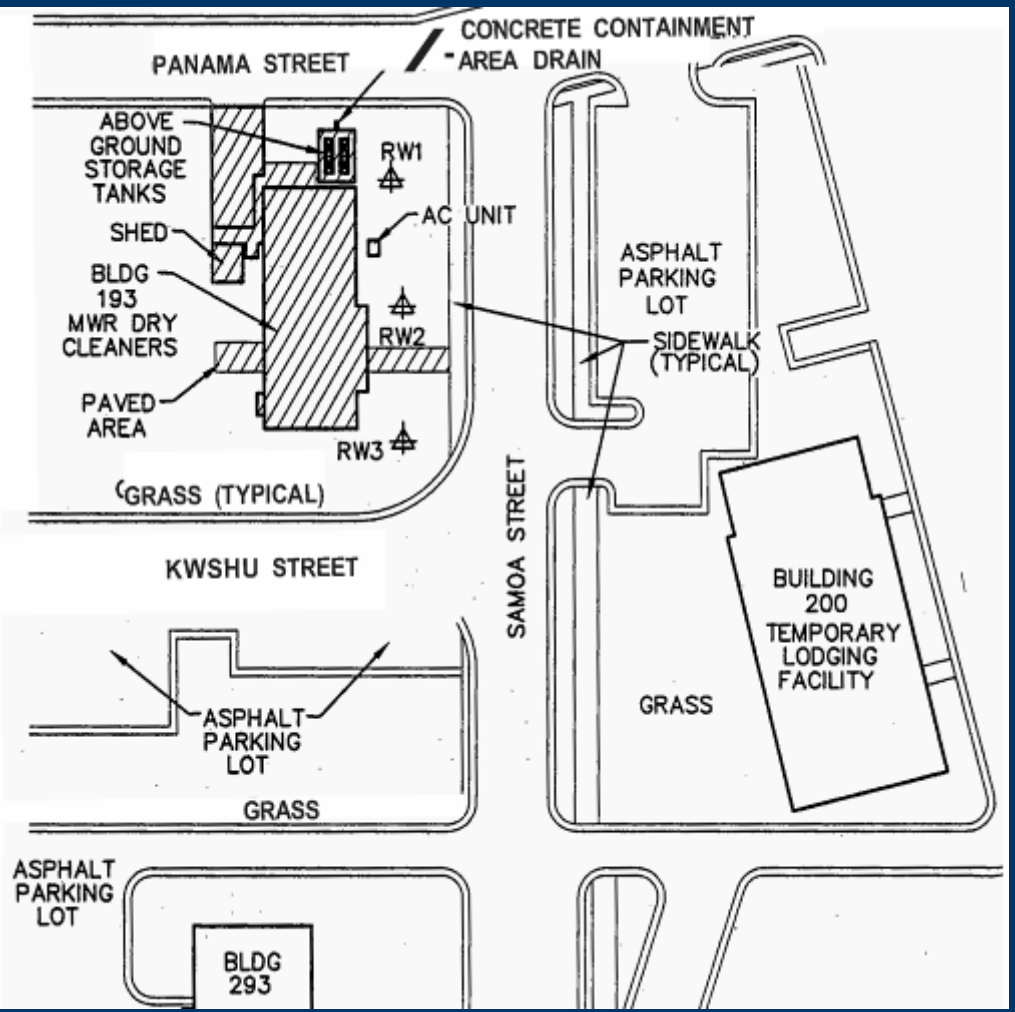
Chloride Production with DNAPL



Conclusions of DNAPL Testing

- Veg Oil Emulsion decreases TCE concentration due to sequestration (no degradation)
- nZVI reduces mass of TCE due to treatment but no decrease in aqueous concentration of TCE (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 then with just the oil; and
  - Reduction in mass of TCE

Demonstration Site
Parris Island MCRD, SC

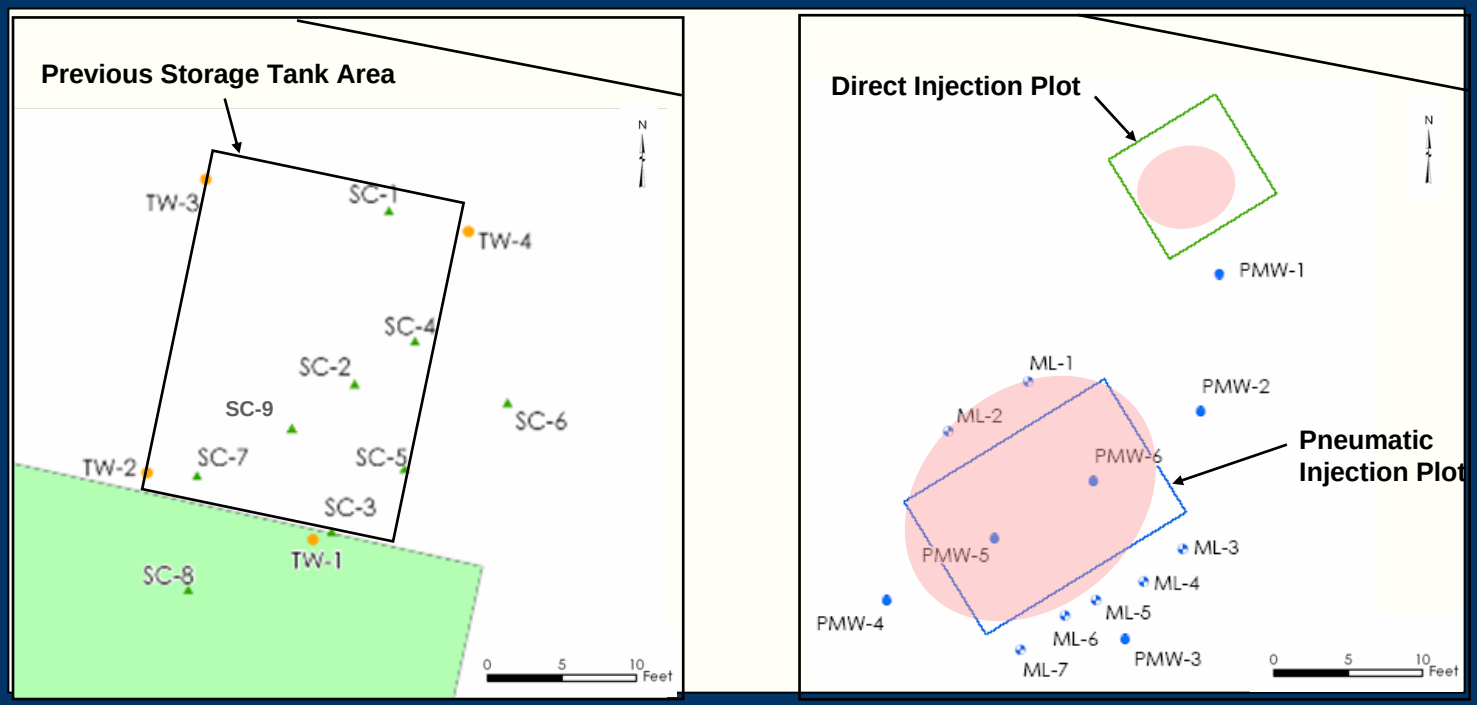


- **Former dry cleaner site**
- **Buildings have been torn down**
- **Source areas located around former above and below ground storage tanks**
- **Evaluate two injection methods and performance assessment of EZVI's ability to degrade VOCs**

Technical Progress

DNAPL Distribution and Well Installation

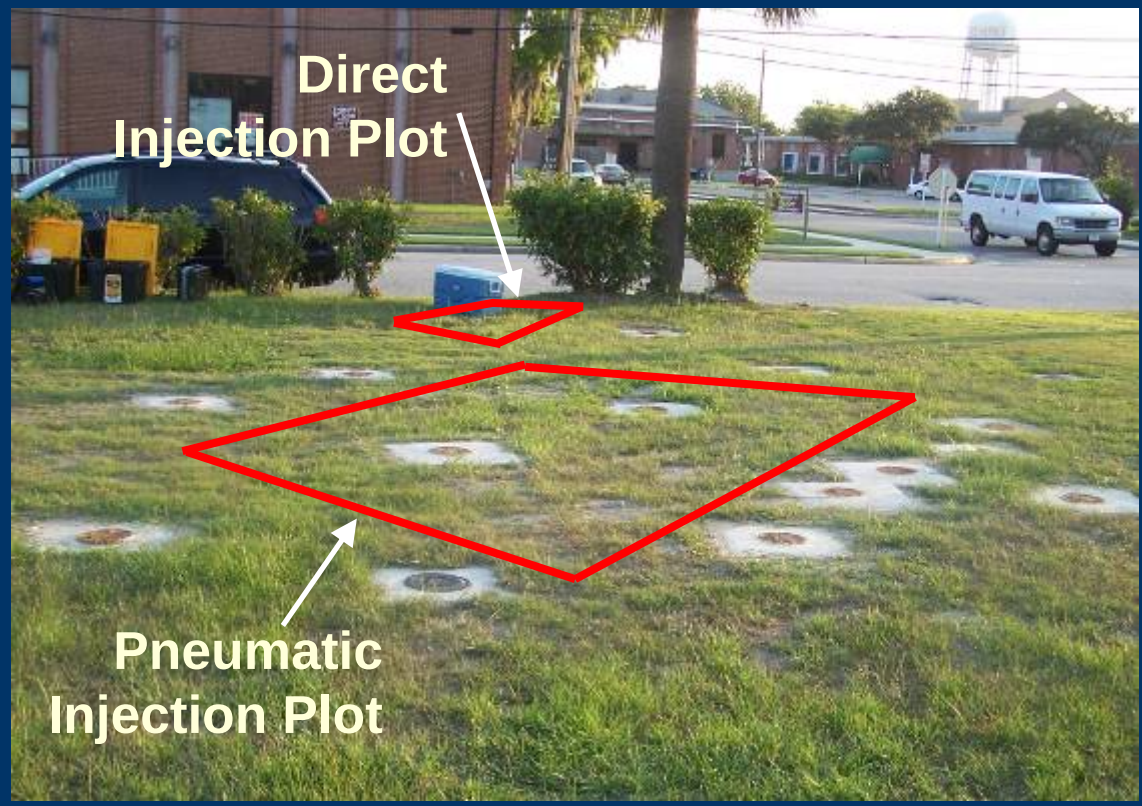
- 9 soil cores and groundwater samples collected in 2005 and 2006 to evaluate contaminant distribution
- Wells installed in July 2006 to target the source areas identified through cores
- EPA (GWERD, National Risk Management Research Laboratory) provided drill rig for coring and well installation



Technical Progress
DNAPL Distribution and Well Installation

Multilevel Well Construction

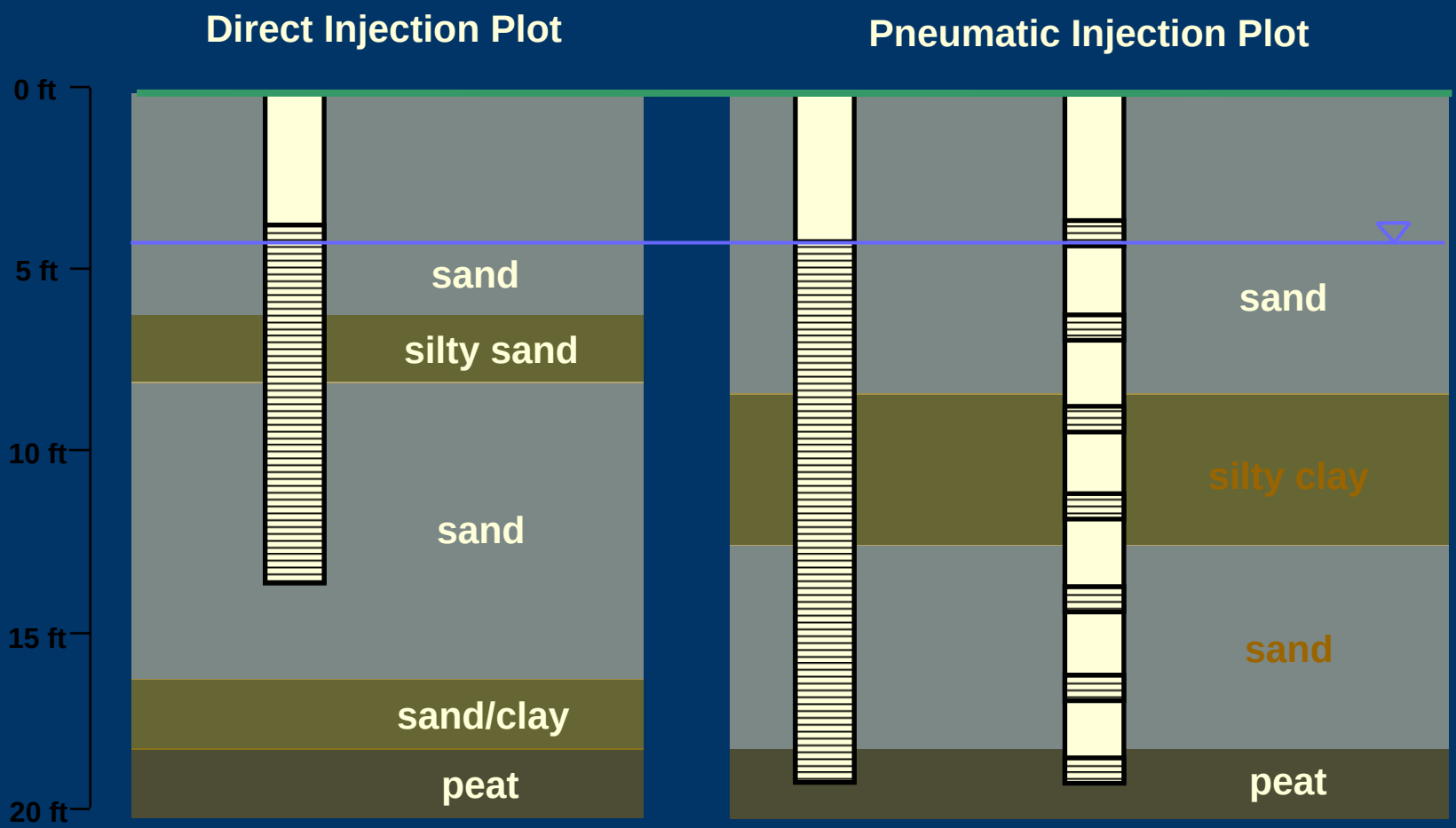
Direct & Pneumatic Injection Plots



Technical Progress

DNAPL Distribution and Well Installation

Fully screened and multilevel wells



Baseline Characterization

Groundwater Sampling

- Groundwater sampling and analysis support provided by EPA
  - EPA personnel participate in all groundwater sampling events and some groundwater samples analyzed at Kerr Laboratories, Ada, OK

- Baseline samples collected from over 50 sample locations (including multilevel wells) during June, August and October 2006 sampling events (2-week sampling events)

- Sample parameters include field parameters (DO, ORP, pH, temperature, conductivity, turbidity) VOCs, DHGs, VFAs, anions, alkalinity, TOC/TIC, metals (dissolved, total), and isotopes (O, H, Cl)

Baseline Characterization

Groundwater Sampling

- DNAPL pumped out of ML-2-5 up-gradient of plot
- Multilevel wells: changes in groundwater mass flux downgradient of plot and evaluate incoming flux to plot (located within a larger plume)
- Fully screened wells: integrated samples within plot for performance evaluation and external to plot to evaluate changes during injection of EZVI

EZVI Preparation

- EZVI made on-site by combining:
  - Nano-scale iron (Toda)
  - Corn oil
  - Surfactant
  - Water
- Ingredients added to drum and mixed using a top mounted industrial mixer
- EZVI pumped from mixing drums into injection tanks

EZVI Injection

Pneumatic Injection Plot

- Total of 575 gal EZVI injected into 8 locations within the Pneumatic Injection Plot between 7 and 19 ft bgs (2 locations using Direct Injection)

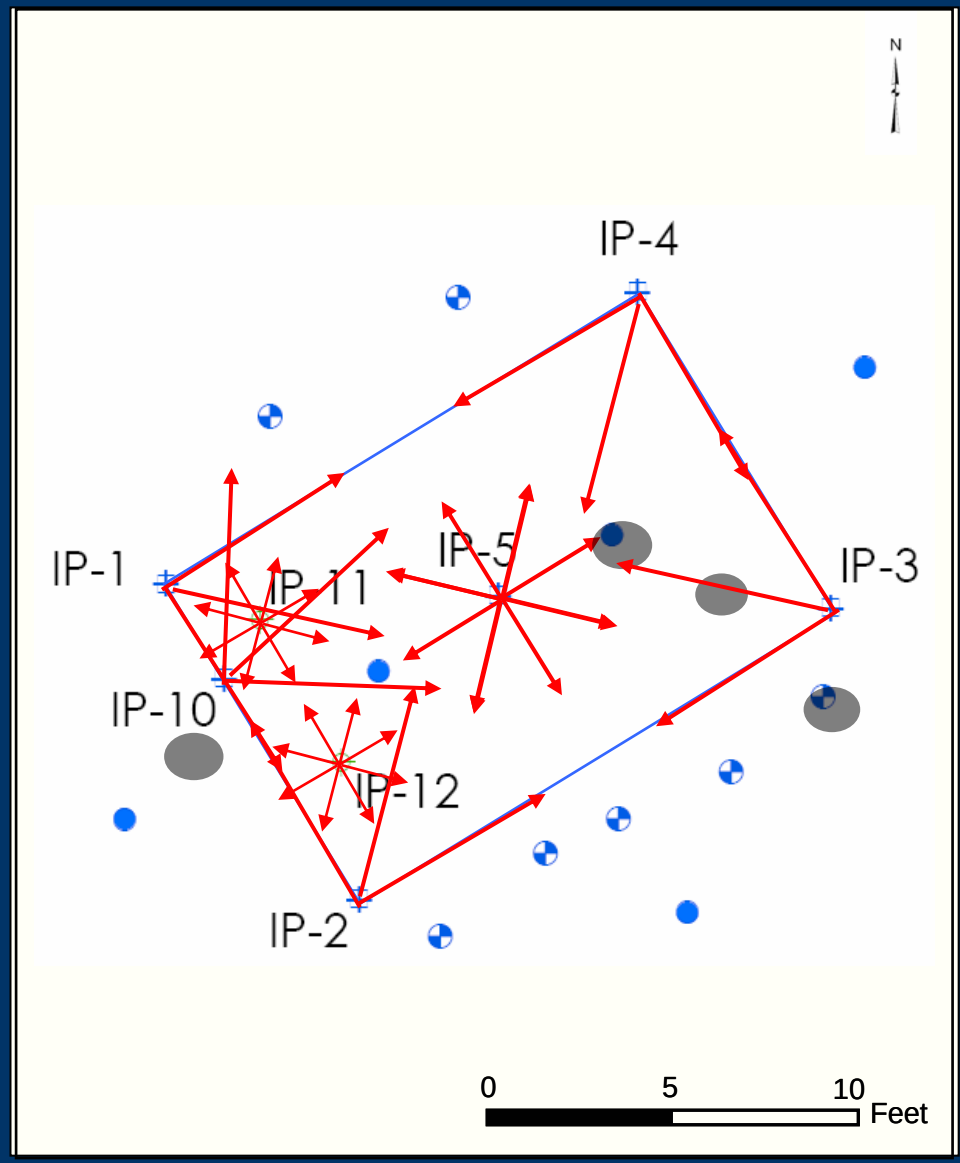
- During injections, monitored injection pressure, pressure distribution in subsurface, ground heave, and looked for EZVI at ground surface

EZVI Injection

Pneumatic Injection Plot

- Total of 575 gal EZVI injected into 8 locations within plot 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 (shown as grey areas on figure)



EZVI Injection

Direct Injection Plot

- Total of 150 gal EZVI injected into 4 locations within plot between 6 and 12 ft bgs

- During injections, monitored injection pressure and looked for EZVI at ground surface

EZVI Injection

Direct Injection

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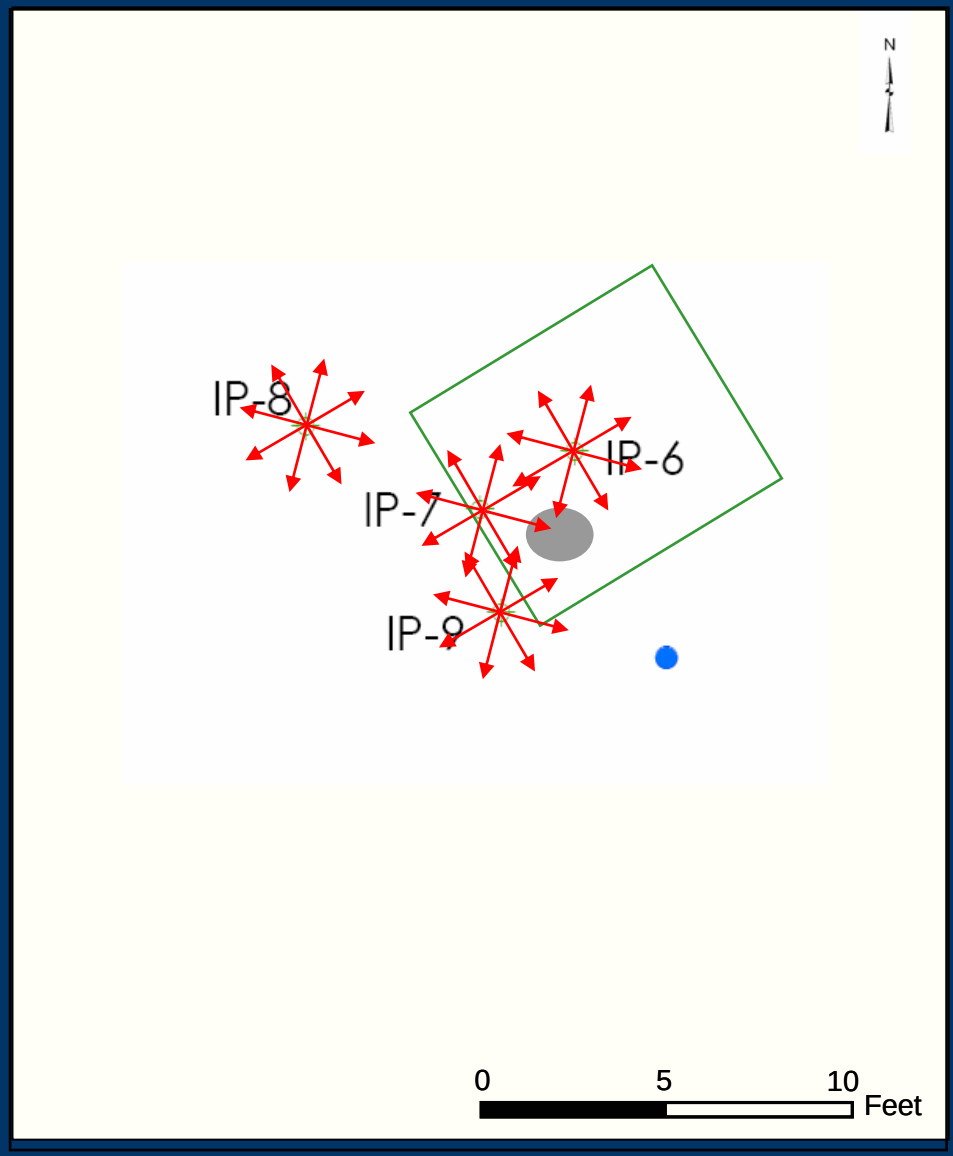


EZVI Injection

- EZVI observed at ground surface in both Pneumatic Injection and Direct Injection Plots

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

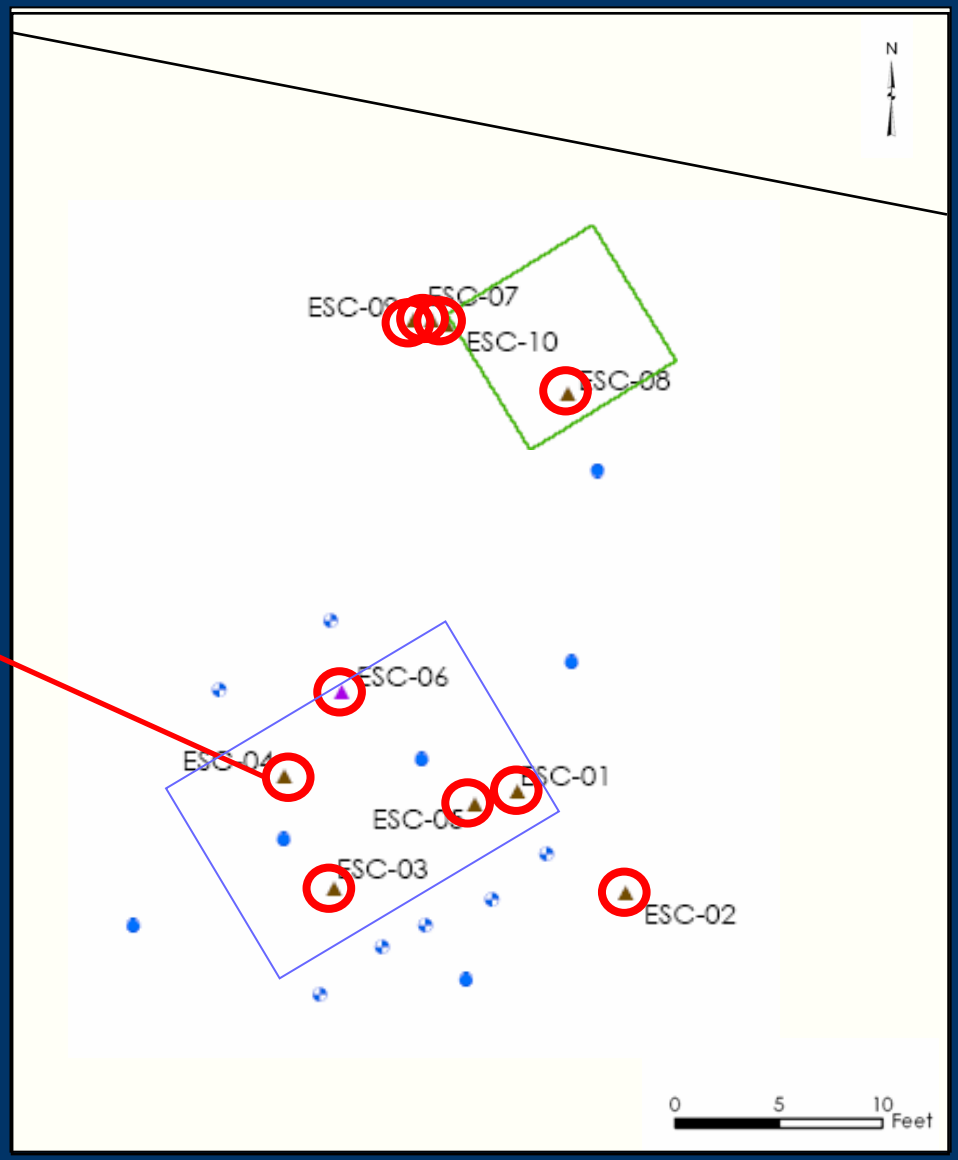
Direct Injection plot (daylighting possibly from old soil core location)

EZVI Injection

EZVI Soil Cores

- Collected cores to evaluate ability of injection technologies to distribute EZVI evenly over the target treatment intervals

sand saturated with EZVI



- Possible EZVI in all soil cores except ESC-06

Performance Monitoring

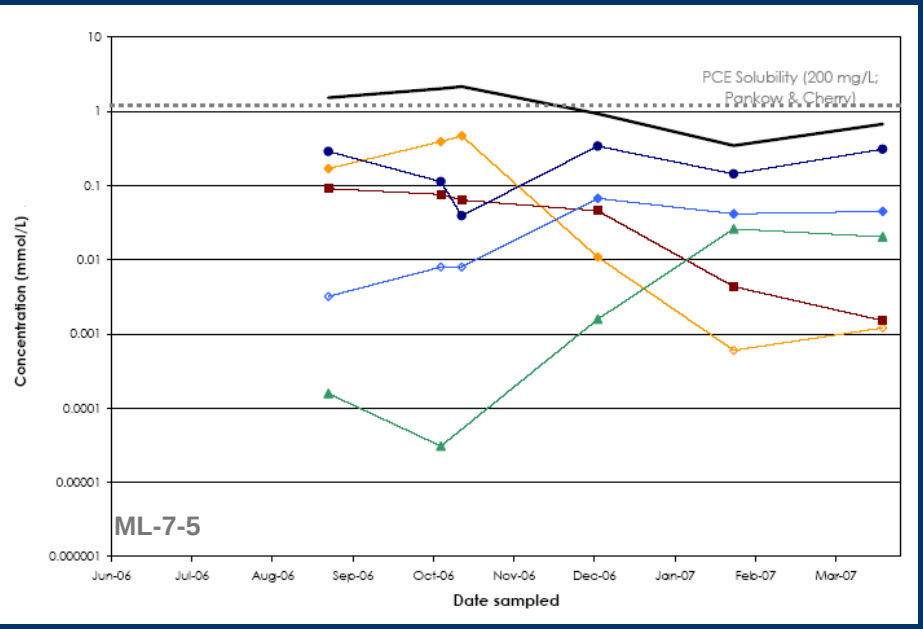
	Parameter	Baseline Samples	Performance Monitoring Samples			Total Samples To Date
		June 2005, June, August & October 2006	November 2006	January 2007	March 2007	
GROUNDWATER	Field Parameters	71	27	32	27	157
	VOCs	136	27	32	27	222
	DHGs	114	27	32	27	200
	VFAs	23	19	4	23	69
	Anions	71	27	32	27	157
	Alkalinity	71	27	32	27	157
	TOC/TIC	71	27	32	27	157
	Metals (dissolved)	71	27	32	27	157
	Metals (total)	71	27	32	27	157
	Isotopes (Cl)	6	-	-	6	12
	Isotopes (O, H)	6	6	6	6	24
SOIL	VOCs	70	-	-	-	70
	EZVI cores (4ft)	32	-	-	-	32
	f_{oc}, porosity	3	-	-	-	3

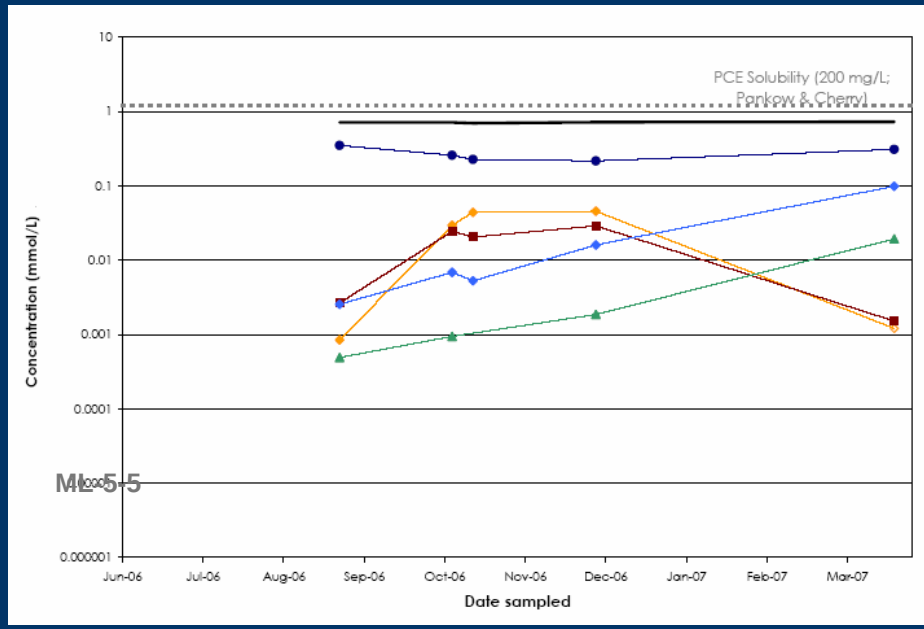
**Sample numbers do not include additional 10% QA/QC samples

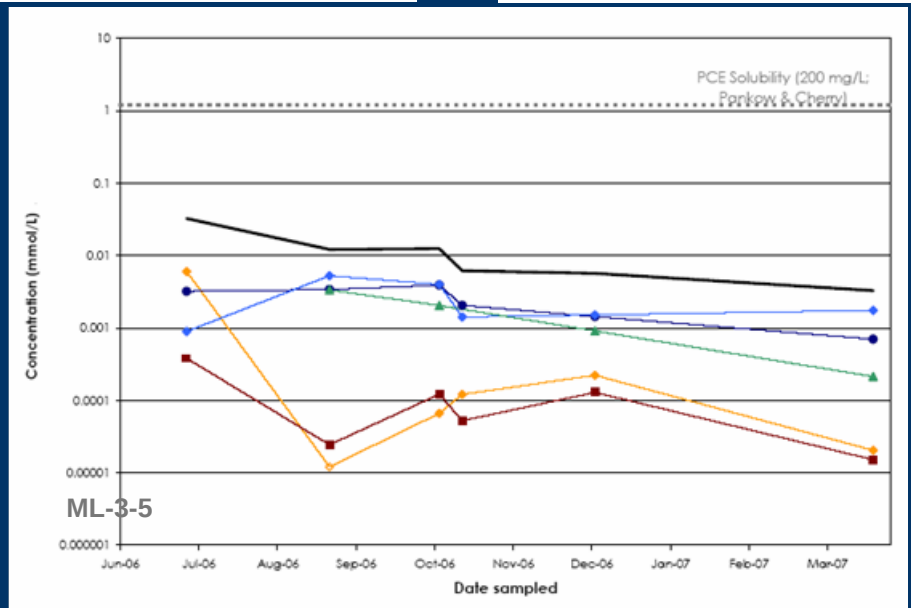
Performance Monitoring
Groundwater Sampling Summary

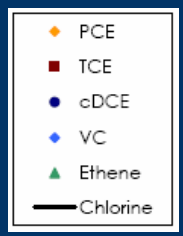
- In general, downgradient wells show decrease in PCE/TCE with increase in degradation products including significant increases in ethene
- Upgradient wells and PMW-5 show continued presence of DNAPL although significant production of ethene in PMW-5 indicates that degradation is ongoing in the area
- Significant increases in VFAs (primarily acetic and propionic acids) and TOC
- Small decrease in pH, and increases in iron (dissolved and total)
- DNAPL now being pumped from ML-2-7 and PMW-5 (inside Pneumatic Injection plot) and from PMW-4 (south [transgradient] of Pneumatic Injection plot) as well as from ML-2-5 where DNAPL was present pre-injection

Performance Monitoring





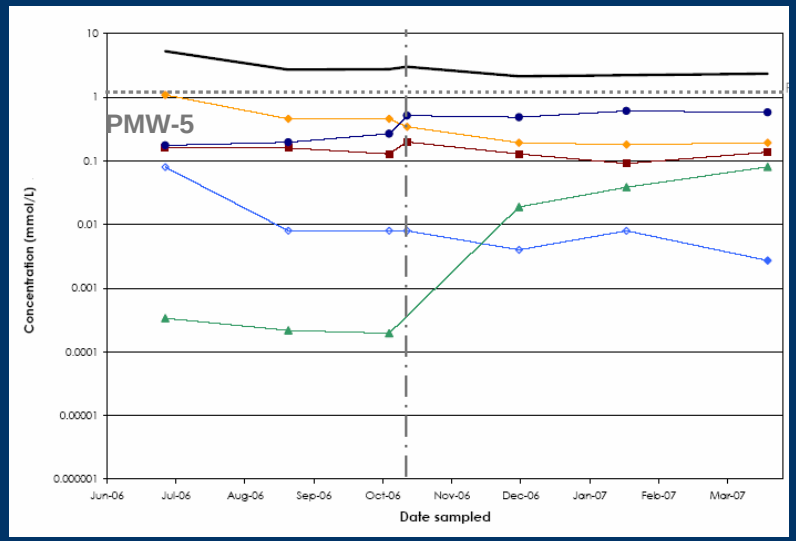


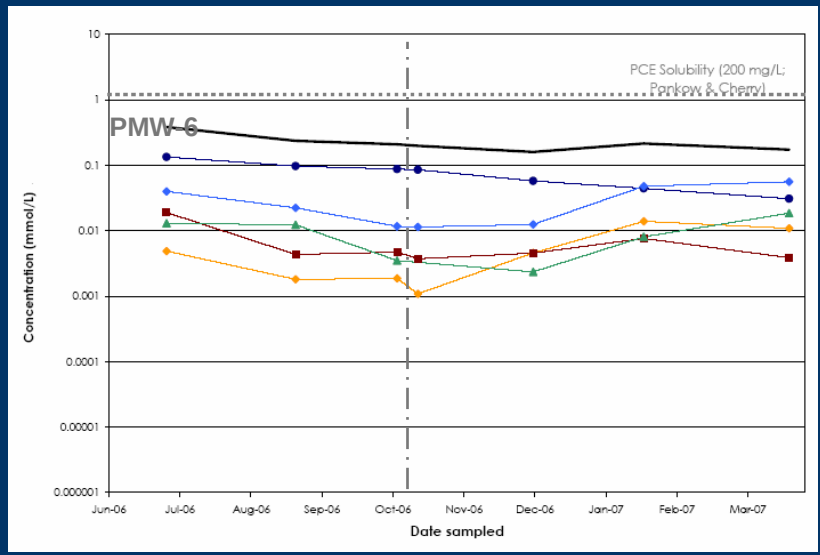


Performance Monitoring

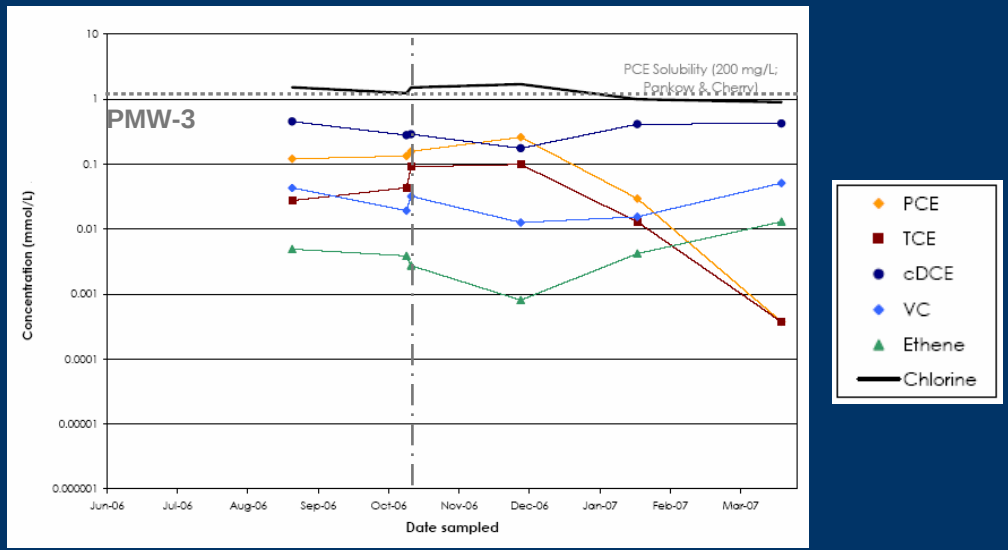
Pneumatic Injection

Interior Wells





Downgradient Well



Next Steps

- Continued monitoring at Parris Island proposed through Oct 09
- Continued use throughout US
- One licensee getting ready for European deployment
- EZVI has taken one private client's site off the NPL

Questions?

EZVI team being inducted into the Space Technology Hall of Fame