A Six-Year Field Test of Emulsified Zero-Valent Iron to Treat Source Zone Chlorinated Solvents at a Superfund Site

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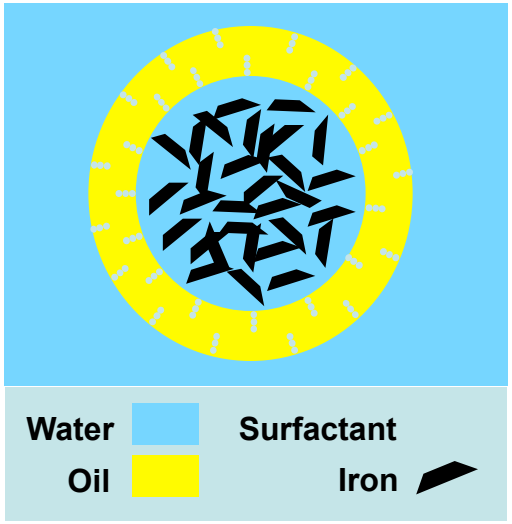

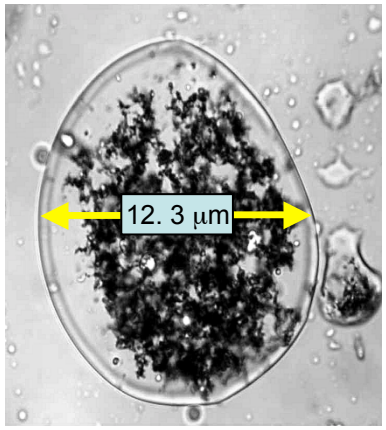

Jacqueline Quinn, NASA

Properties of Emulsified Zero-Valent Iron (EZVI)

- Emulsion droplets contain nanoscale zero-valent iron (ZVI) particles in water surrounded by an oil-liquid membrane (food-grade surfactant, biodegradable vegetable oil)
- Oil layer of emulsion is miscible with the DNAPL
- Chlorinated volatile organic compounds (CVOCs) diffuse through the oil membrane and are degraded in the presence of the ZVI in the interior aqueous phase
- EZVI can be used to enhance degradation of DNAPL by enhancing contact between the DNAPL and the ZVI particles
- Due to vegetable oil and surfactant which will act as long-term electron donors, EZVI also promotes anaerobic biodegradation

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Objectives

- To evaluate two injection technologies (pneumatic and direct injections) within a DNAPL source zone for EZVI delivery
- To evaluate the effectiveness of EZVI to decrease mass flux of dissolved volatile organic compounds (VOCs) from a DNAPL source zone and decrease the DNAPL mass in the source area
- To investigate fate and transport of injected nanoscale ZVI

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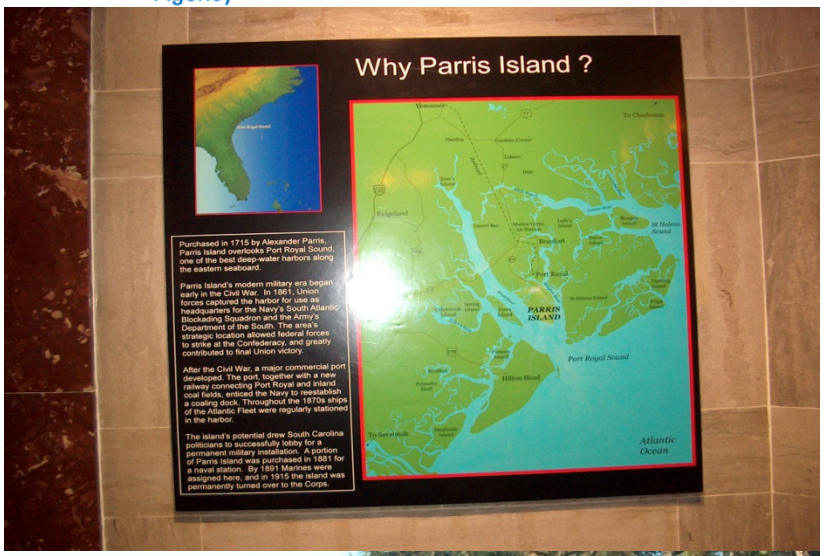

Reasons for Selecting Parris Island site:

- Free phase DNAPL
- Easy access
- Site support available

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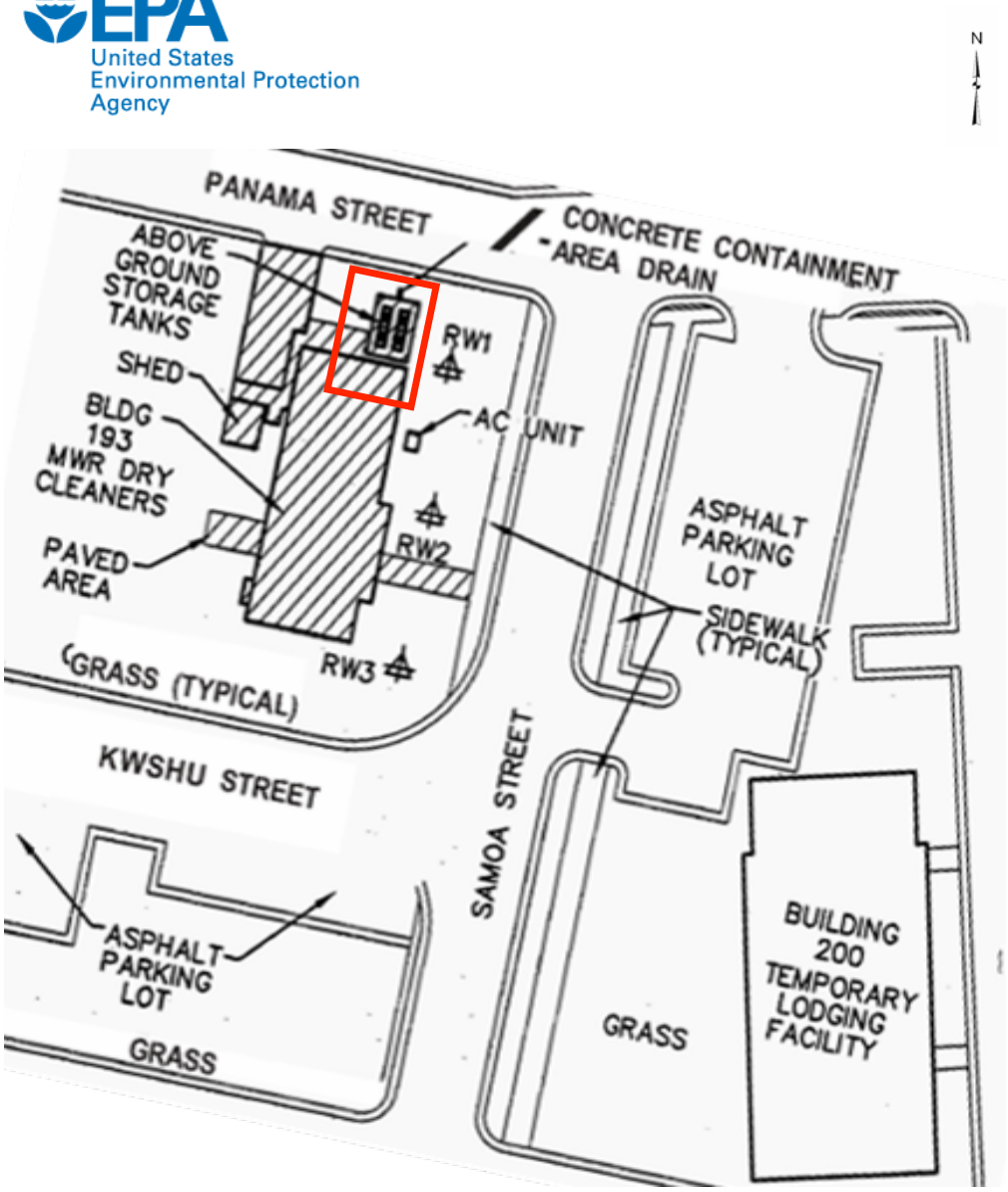

Demonstration Site

Marine Corps Recruit Depot
Parris Island, SC

Former dry cleaner facility

Buildings torn down

Source areas located around former above- and below-ground storage tanks

Tetrachloroethene (C_2Cl_4,PCE)
Spill in 1994

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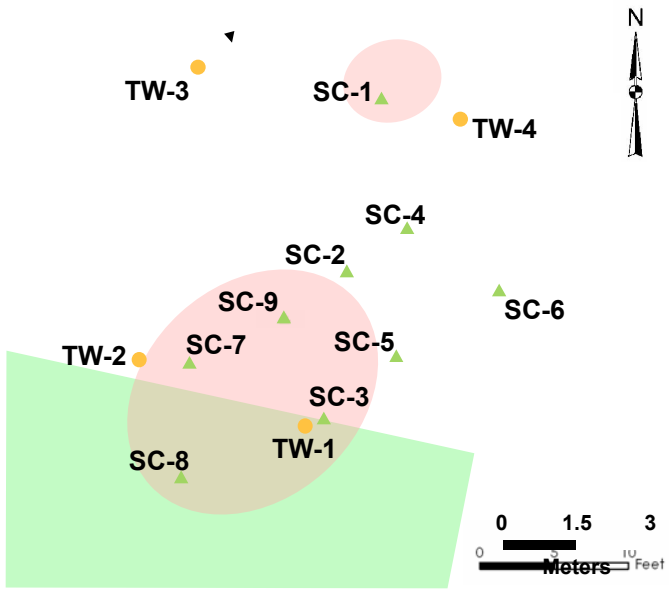
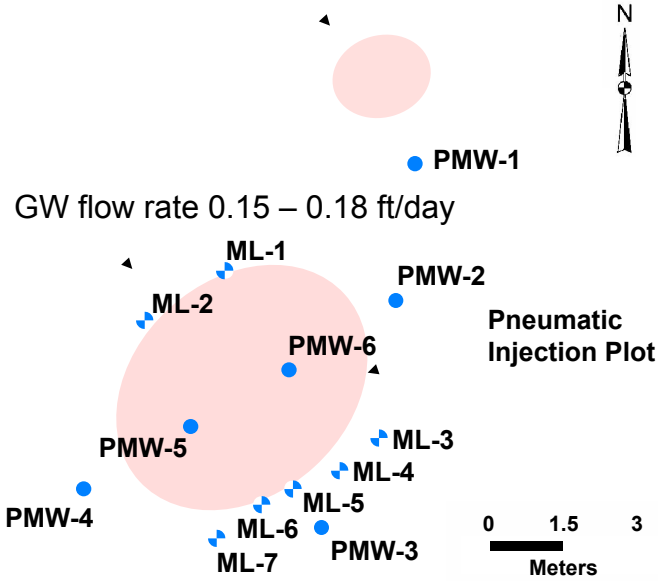
- 9 soil cores and groundwater samples collected in 2005 and 2006 to evaluate contaminant distribution
- Wells installed in June 2006 to target the source areas identified through cores

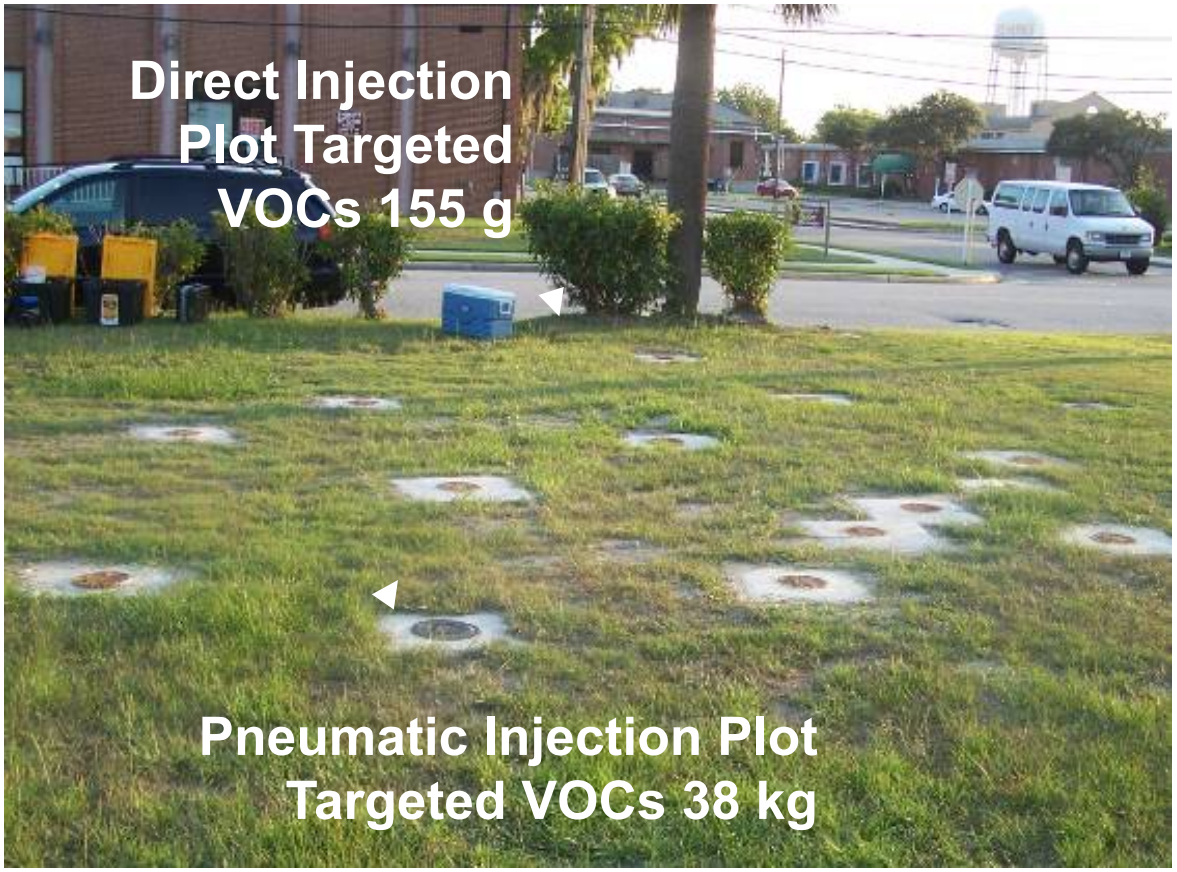
Previous Storage Tank Area



Direct Injection Plot



Monitoring Well Installation



Multilevel Well Construction

Direct and Pneumatic Injection Plots

Baseline Characterization

- Samples collected from over 50 sample locations (including multilevel wells) during June, August, and October 2006 sampling events
- Sample parameters include field parameters (DO, ORP, pH, conductivity, turbidity), CVOCs, DHGs, VFAs, anions, alkalinity, TOC/TIC, metals (dissolved, total), and isotopes (C-13, Cl-37)
- Integral pump test performed downgradient of Pneumatic Injection test plot

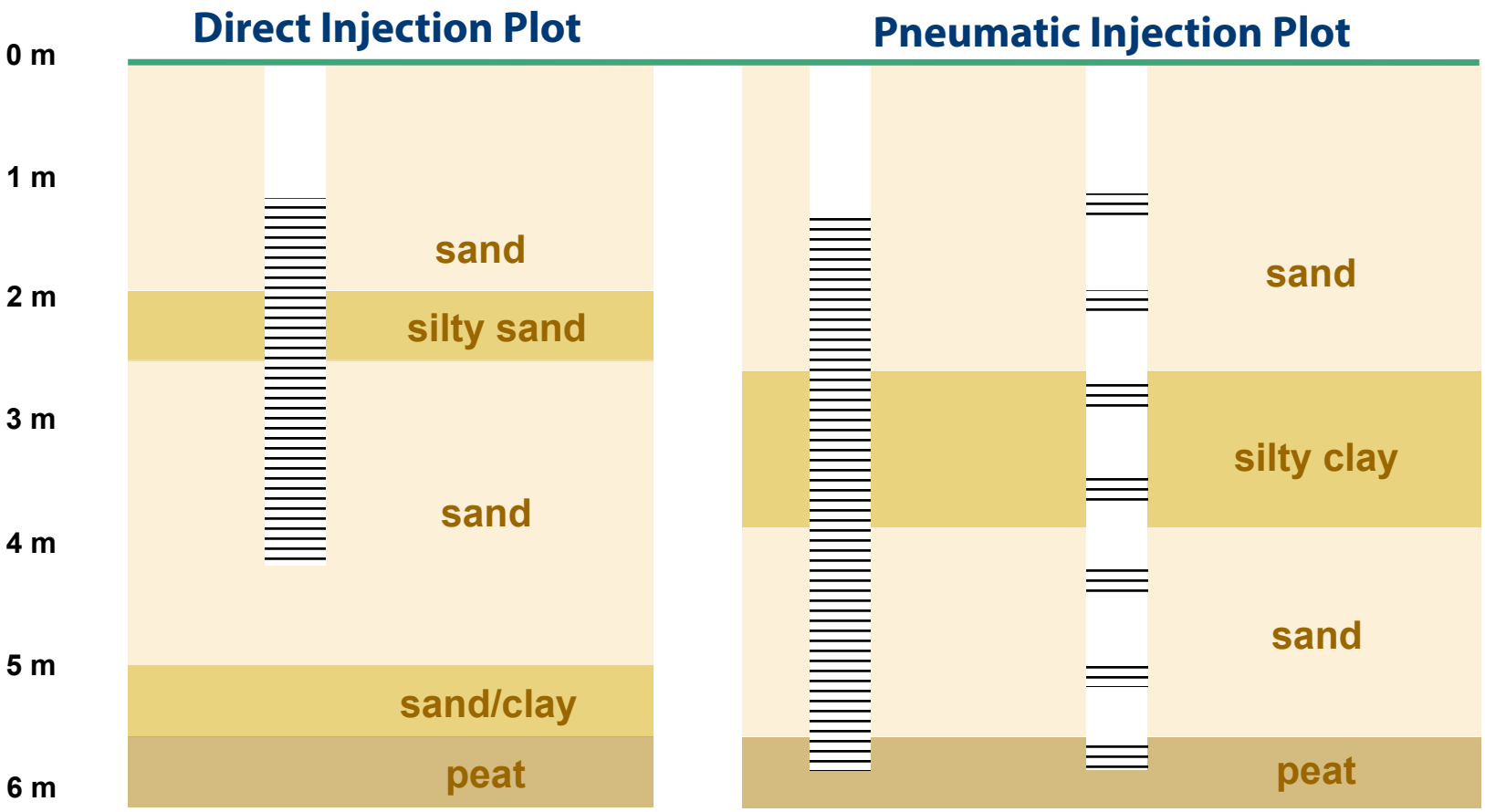
DNAPL

EZVI Preparation

- EZVI made on-site by combining:
  - Nanosized iron (Toda, 35-140 nm, $1 lb) 10% by weight
  - Corn oil 38%
  - Surfactant (Sorbitan Trioleate) 1%
  - Tap water 51%
- Ingredients added to drum and mixed using a top mounted industrial mixer
- EZVI pumped from mixing drums into injection tanks

Demonstration Site

Fully screened and multilevel wells



Target zone: 2-3.5 m bgs

Target zone: 2-6 m bgs

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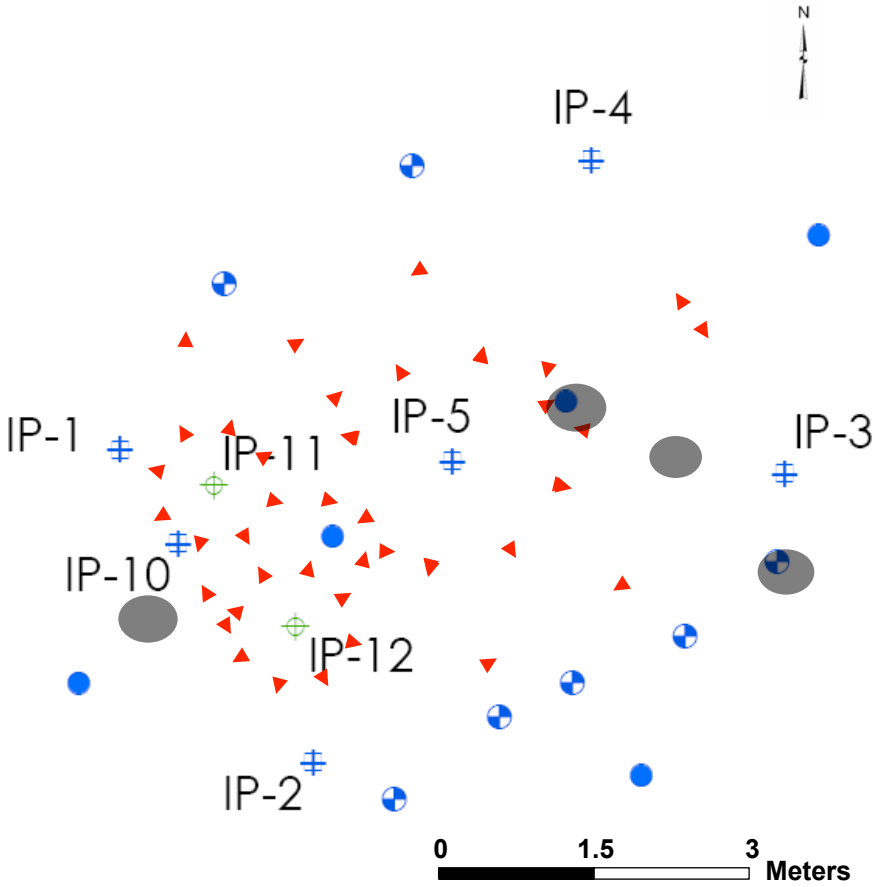
EZVI Injections

Pneumatic Injection Plot

- 575 gal EZVI injected at 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)



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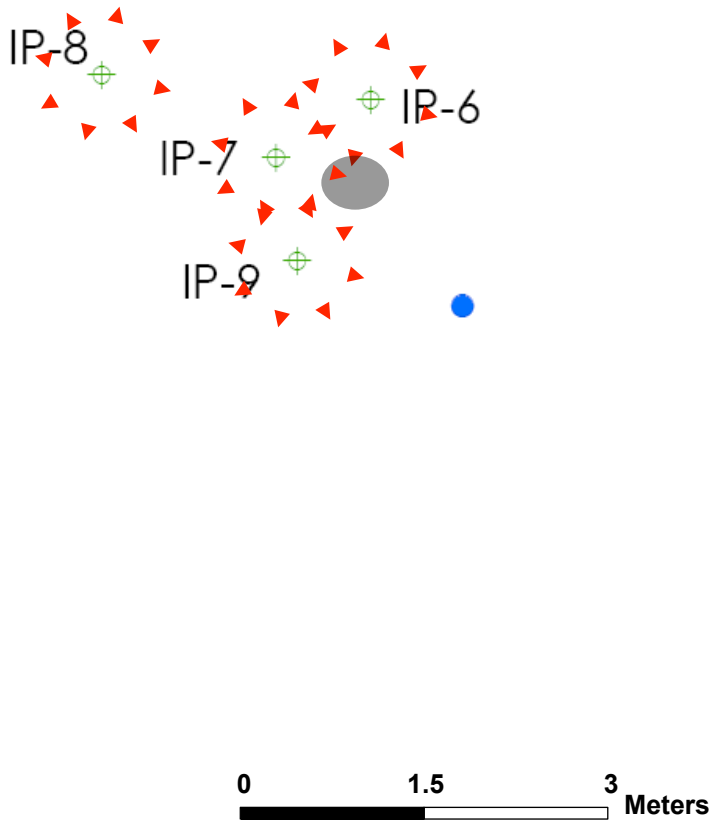
EZVI Injections

Direct Injection Plot

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



EZVI Injection

EZVI daylighted in both Pneumatic Injection and Direct Injection Plots

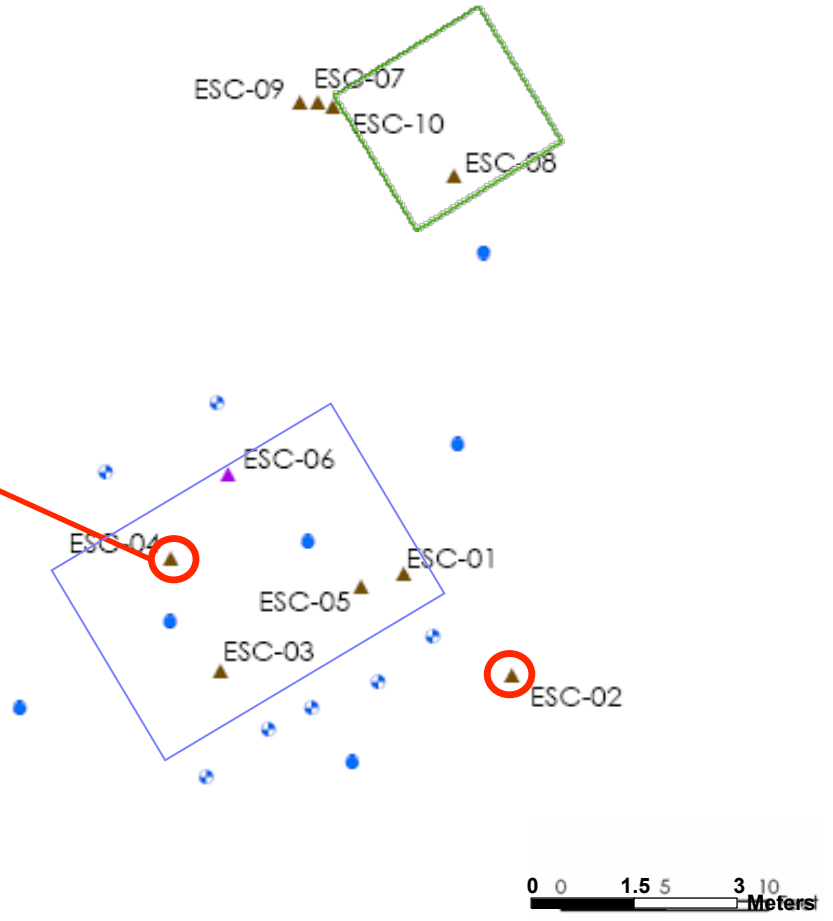
Pneumatic Injection plot (daylighting around ML-3 pad, down-gradient of plot)

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

EZVI Soil Cores

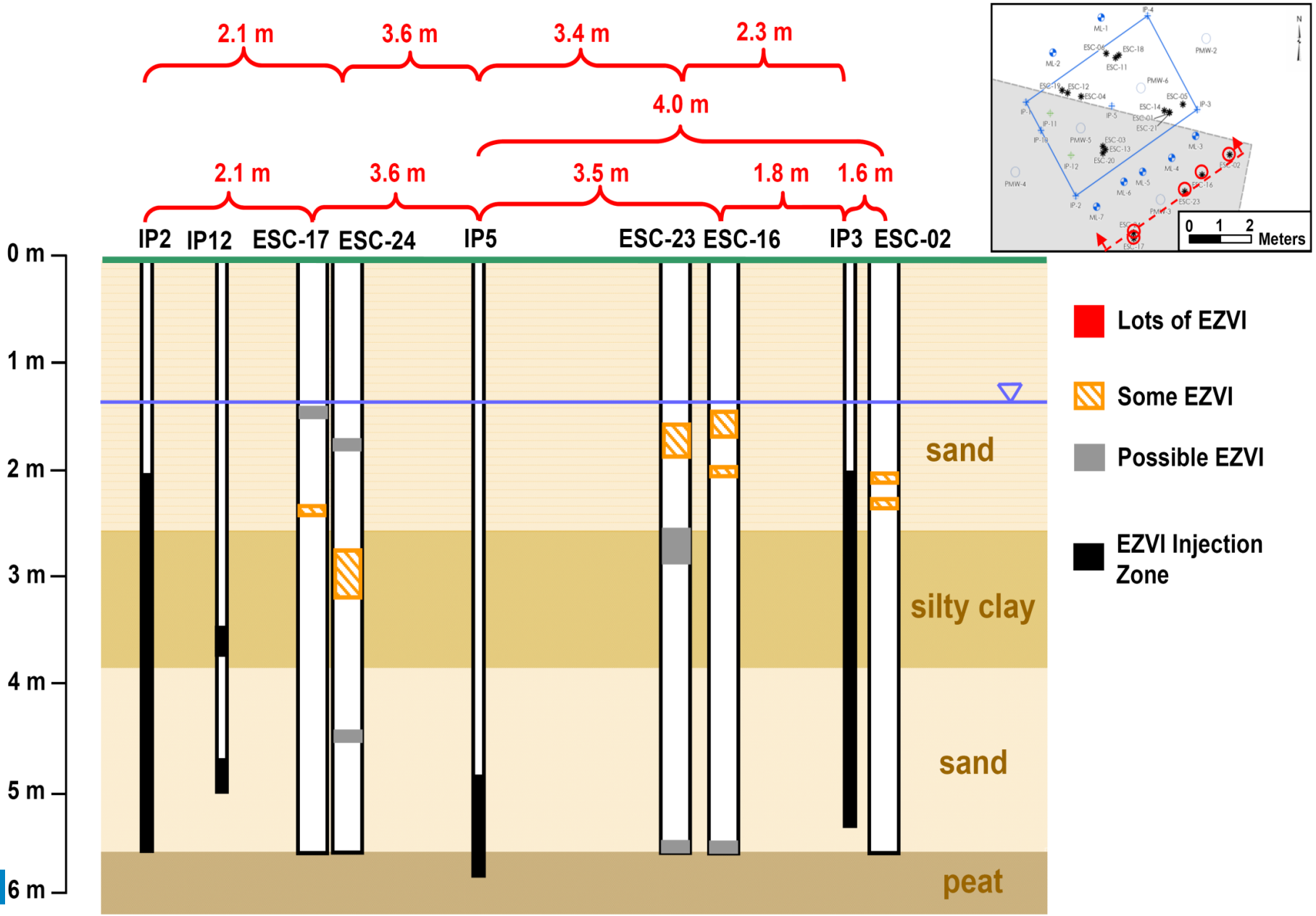
- Collected cores to evaluate ability of injection technologies to distribute EZVI evenly over the target treatment intervals

Sand saturated with EZVI

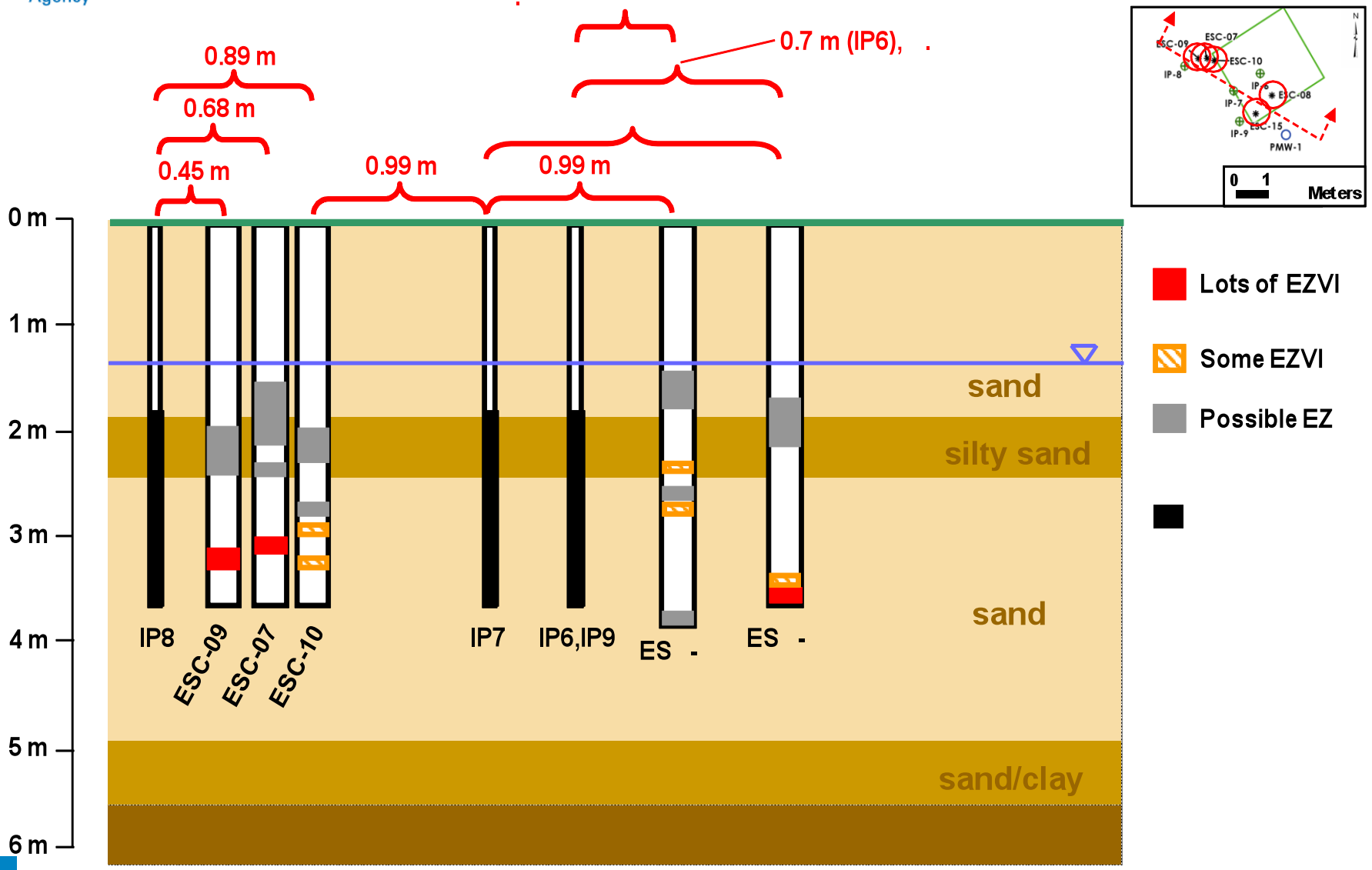


- EZVI was observed in all soil cores with the possible exception of ESC-06
- The most conservative estimate of travel distance was made by using the closest injection points as the assumed point of origin.

EZVI Soil Cores (Pneumatic Injection Plot)



EZVI Soil Cores (Direct Injection Plot)



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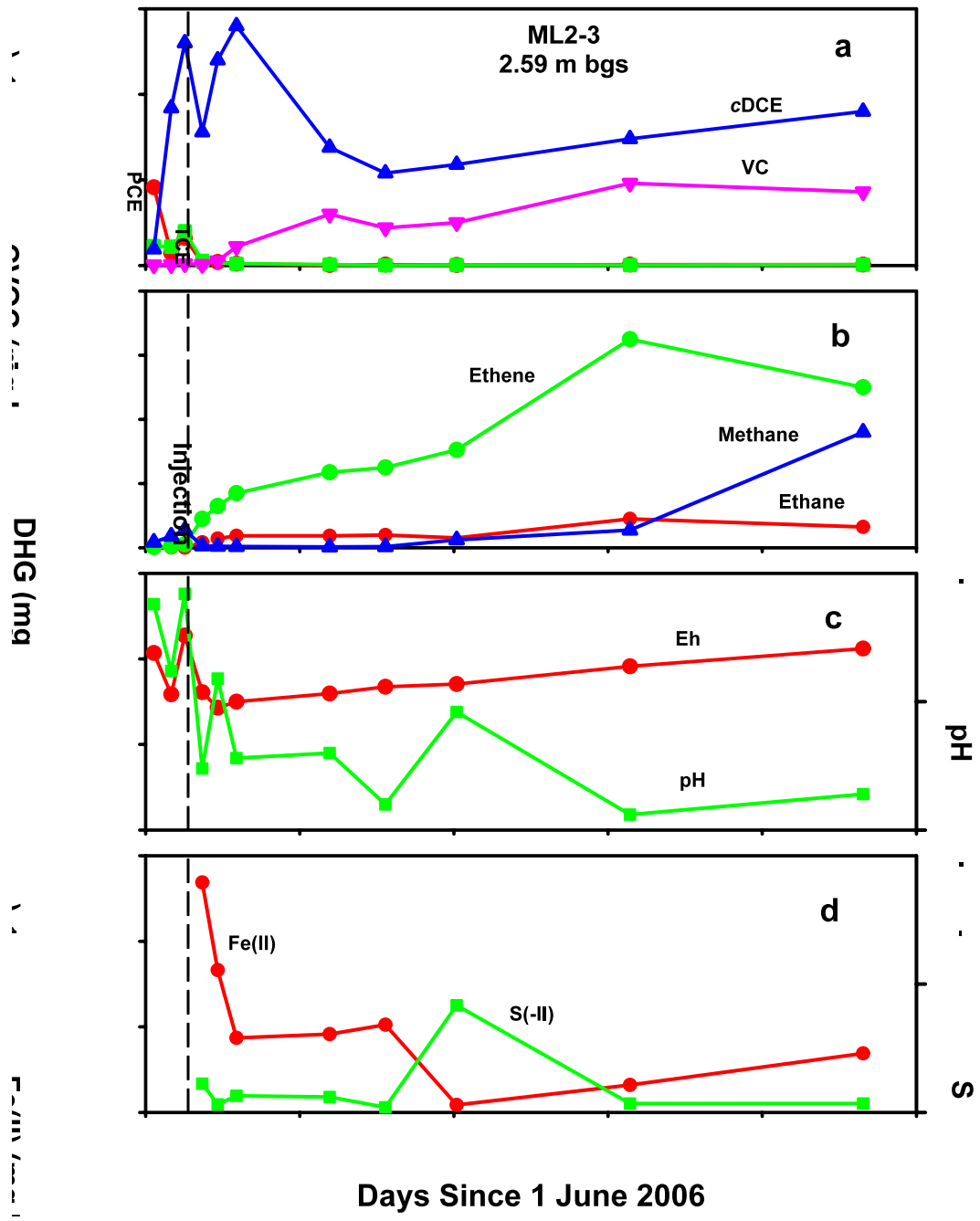
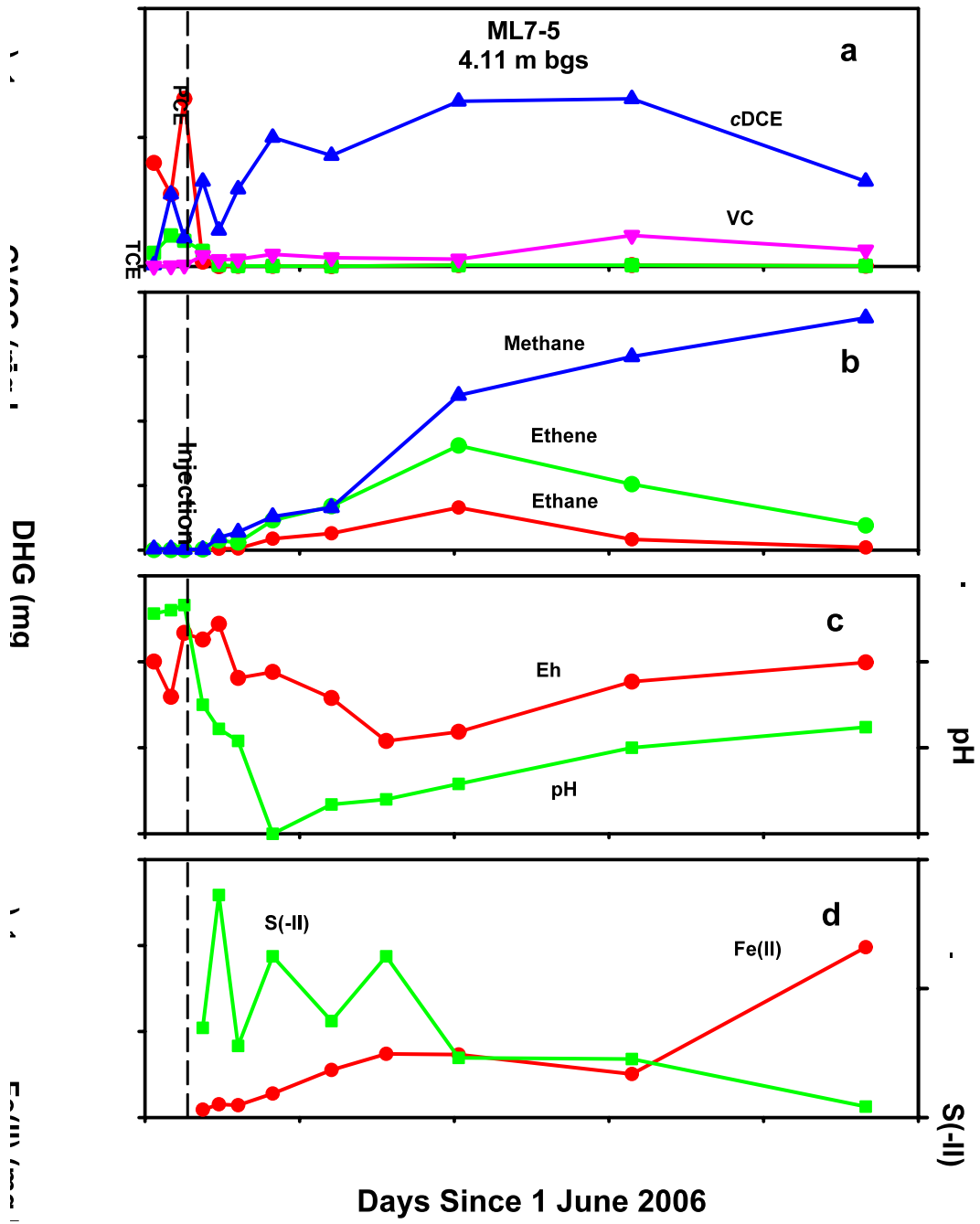
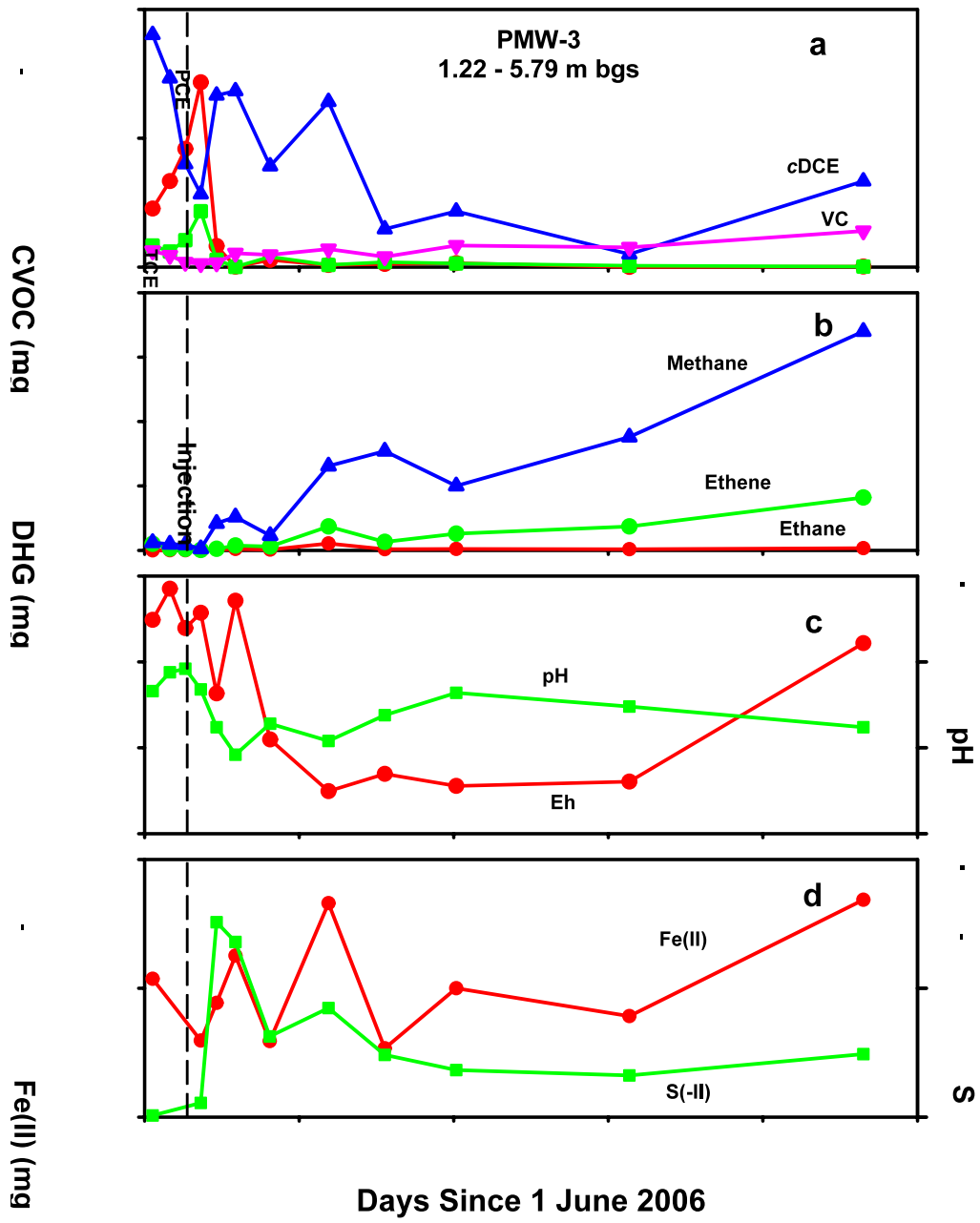
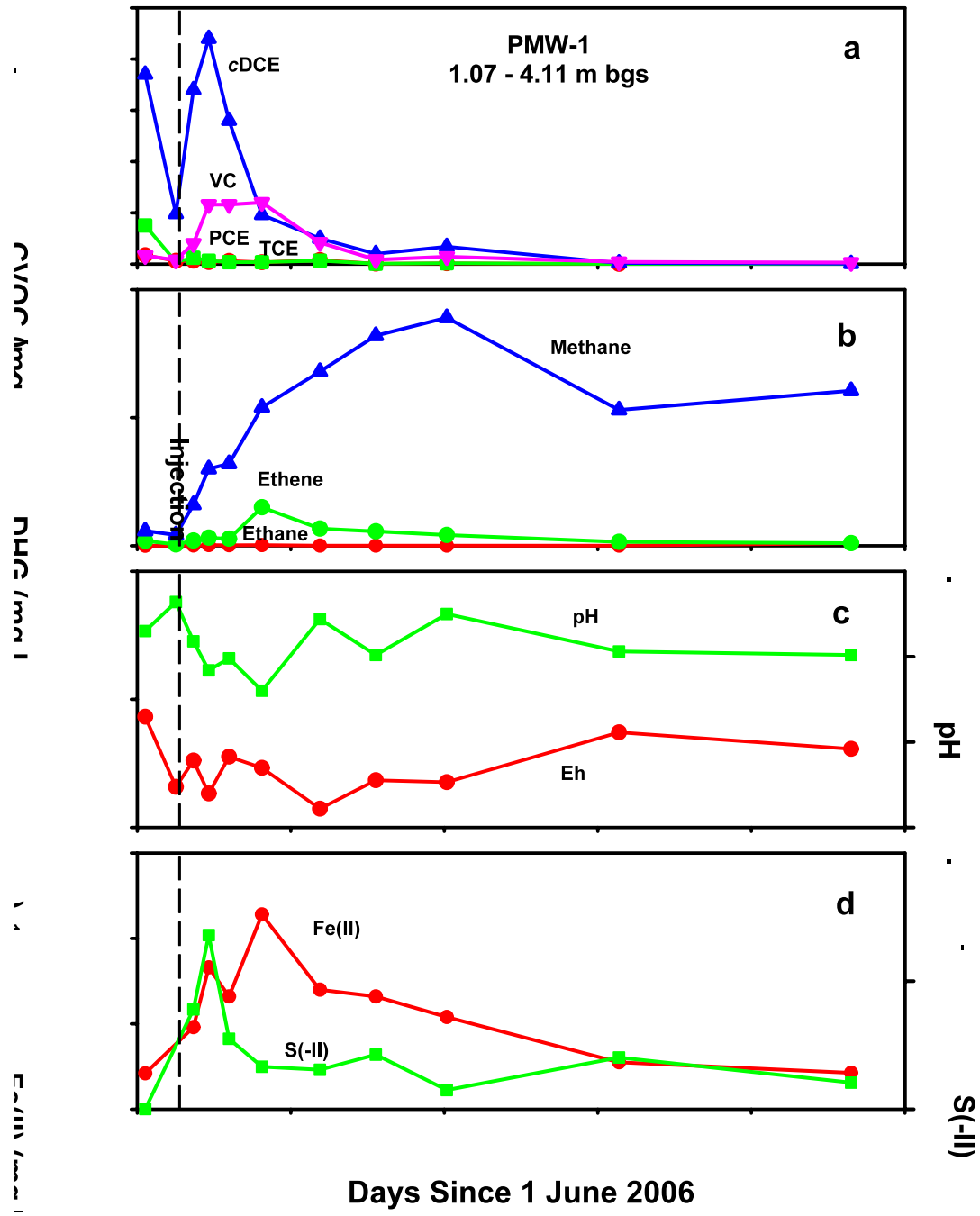
Performance Monitoring

- Samples collected from same locations as baseline sampling events; samples collected in November 2006; January, March, and July 2007; and January, July 2008; March 2009; September, October 2010; October 2012 (2-3 week sampling events)
- Samples analyzed for the same parameters as baseline events

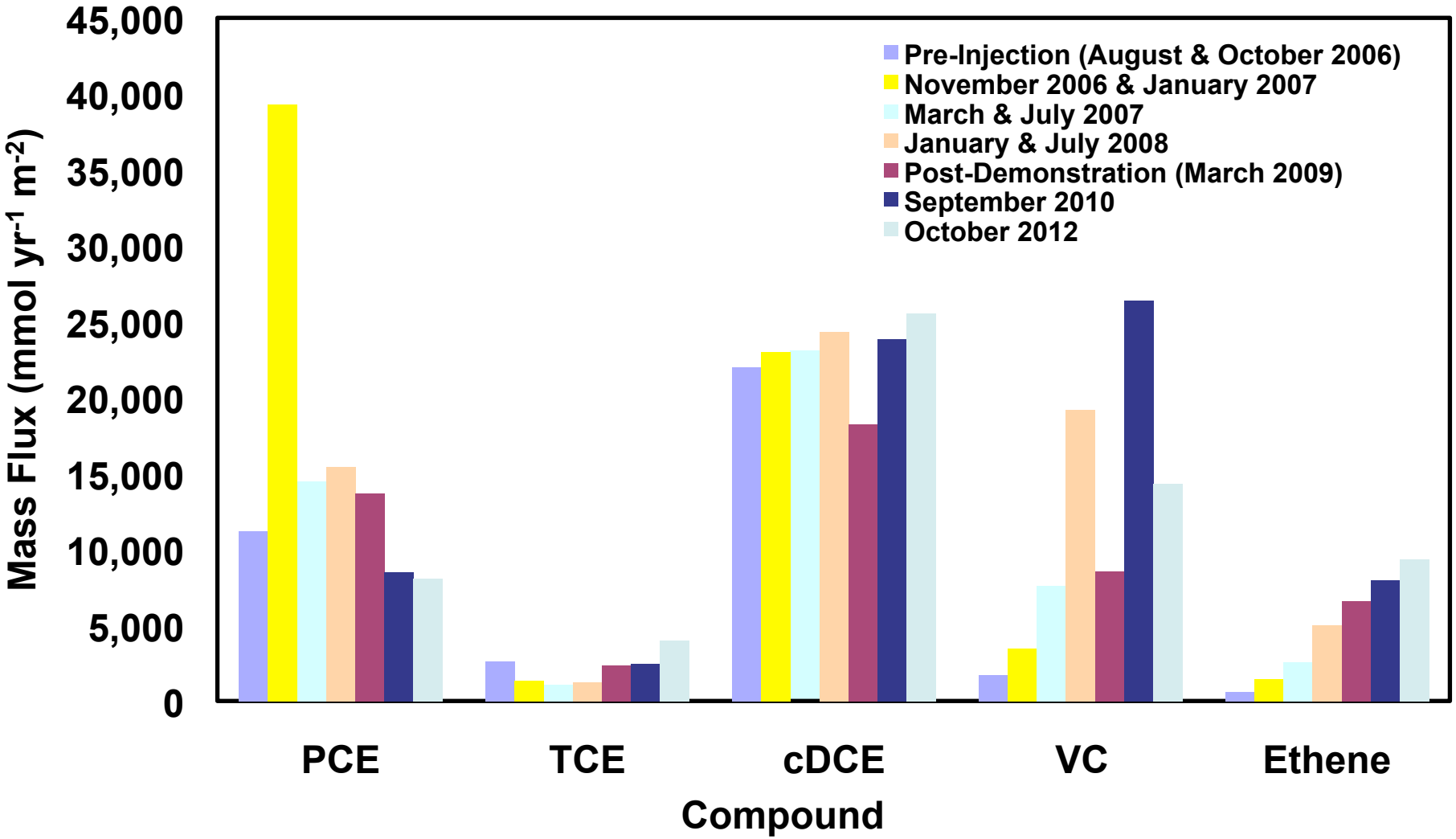

ML2-3
2.59 m bgs
a
cDCE
VC
PCE
TCE
b
Ethene
Methane
Ethane
Injection
c
Eh
pH
d
Fe(II)
S(-II)
DHG (mg
pH
S
Days Since 1 June 2006


ML7-5
4.11 m bgs
a
PCE
TCE
cDCE
VC
b
Methane
Ethene
Ethane
Injection
c
Eh
pH
d
S(-II)
Fe(II)
DHG (mg
pH
S(-II)
Days Since 1 June 2006

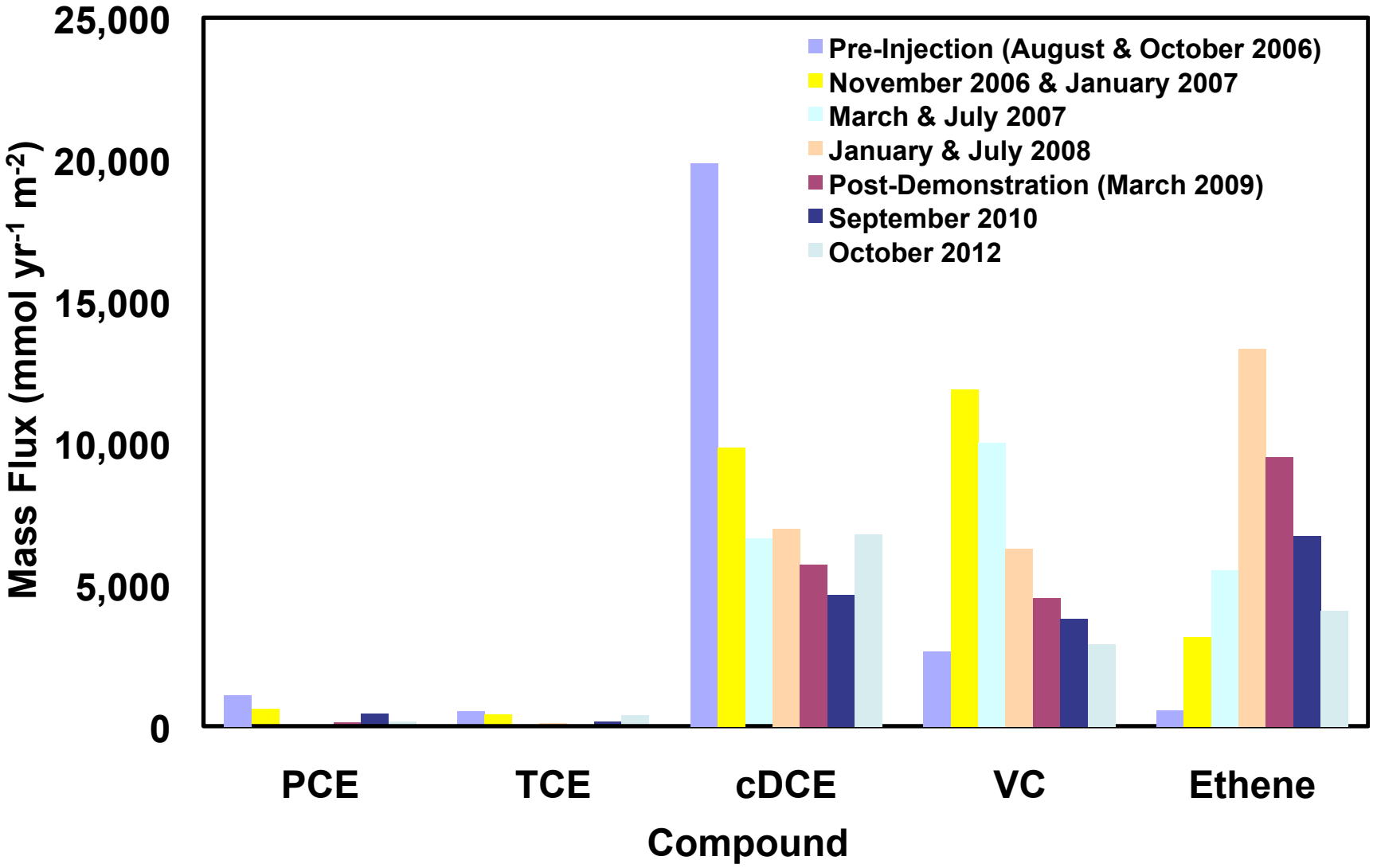

PMW-3
1.22 - 5.79 m bgs
a
PCE
TCE
cDCE
VC
b
Methane
Ethene
Ethane
Injection
c
pH
Eh
d
Fe(II)
S(-II)
CVOC (mg
DHG (mg
Fe(II) (mg
pH
S
Days Since 1 June 2006


PMW-1
1.07 - 4.11 m bgs
a
cDCE
VC
PCE
TCE
b
Methane
Ethene
Ethane
Injection
c
pH
Eh
d
Fe(II)
S(-II)
pH
S(-II)
Days Since 1 June 2006

Upgradient Mass Flux Estimates Based on Wells ML-1 and ML-2



Downgradient Mass Flux Estimates Based on Wells ML-3 and ML-7



Pre- and Post-demonstration CVOC Mass Estimates in Pneumatic Injection Plot

Media	VOC	Pre-Injection Mass (g)			Post-demonstration Mass (g)		
		Sorbed/Dissolved	DNAPL	Total	Sorbed/Dissolved	DNAPL	Total
Soil	PCE	2,760	29,028	31,788	3,116	1,384	4,500
	TCE	1,317	0	1,317	672	0	672
	Cis-DCE	1,254	0	1,254	1,542	0	1,542
	VC	2,214	0	2,214	204	0	204
Groundwater	PCE	577	0	577	48	0	48
	TCE	267	0	267	50	0	50
	Cis-DCE	588	0	588	1,226	0	1,226
	VC	12	0	12	103	0	103
Total Mass (g)		8,990	29,028	38,018	6,962	1,384	8,346
% Reduction					23%	95%	78%

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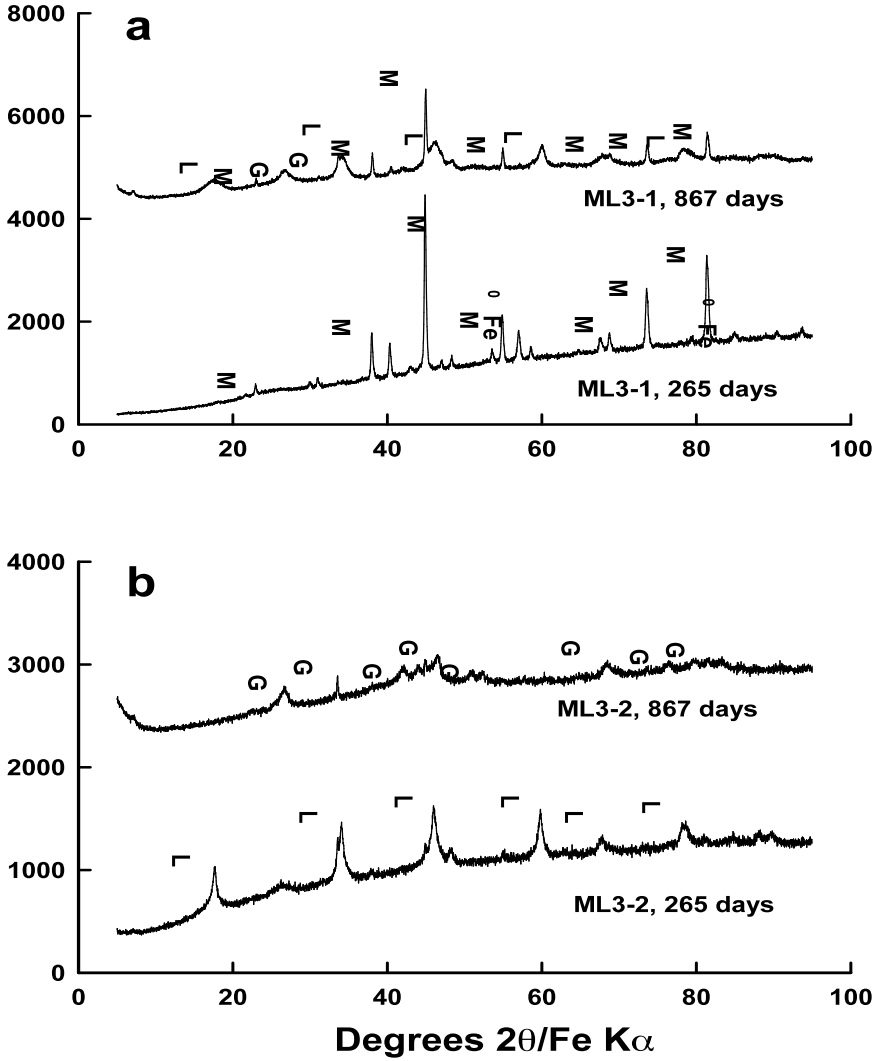
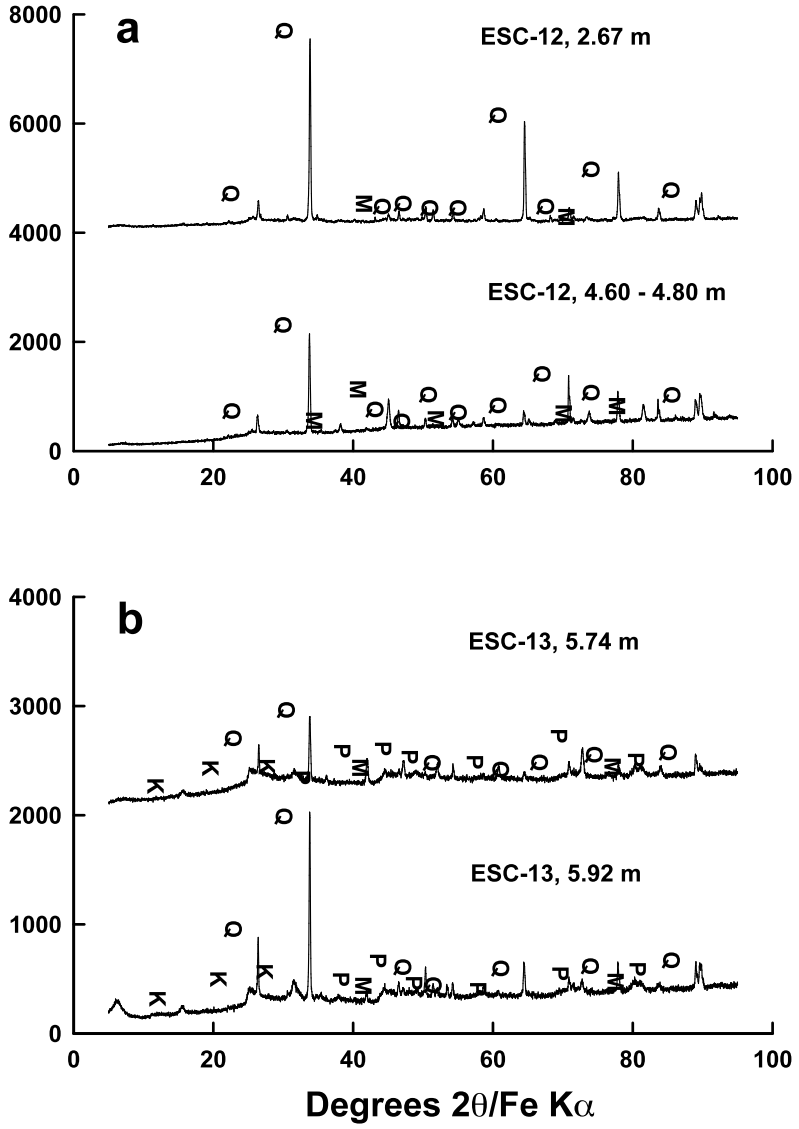
X-ray Diffractograms of Solids from Well Purge Water



Fe^0: α-Fe^0
M: Magnetite (Fe_3O_4)
L: Lepidocrocite (γ-FEOOH)
G: Goethite (α-FeOOH)

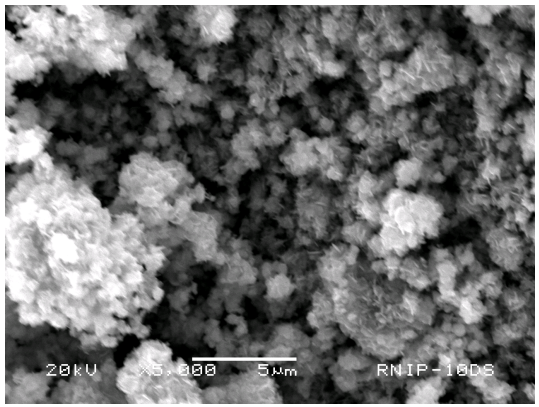
X-ray Diffractograms of Soil Cores (2.5 Years After Injection)



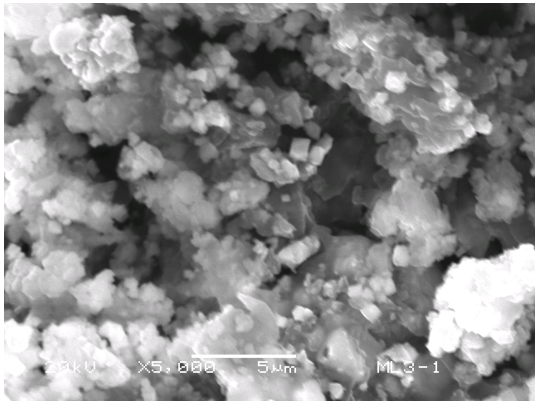
Q: Quartz (SiO_2)
K: Kaolinite ($Al_2Si_2O_5(OH)_4$)
P: Pyrite (FeS_2)
M: Magnetite (Fe_3O_4)

Scanning Electron Microscopy

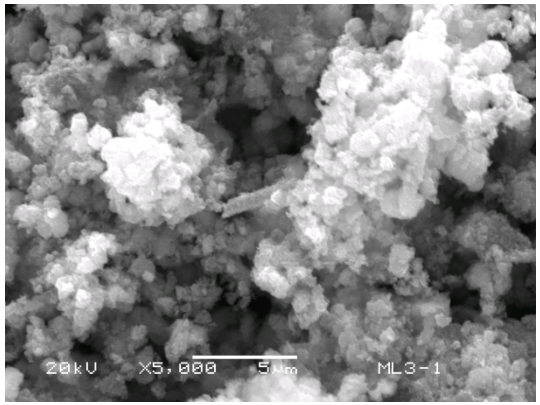
a: RNIP-10DS, Aged 8 days



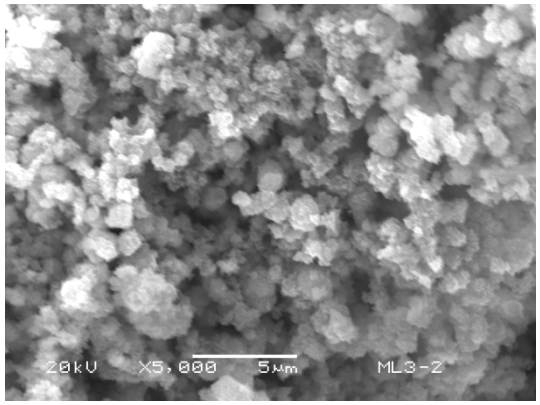
b: ML3-1, 7/7/07



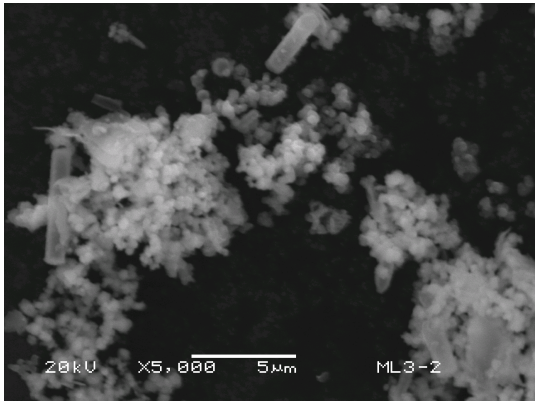
c: ML3-1, 3/3/09



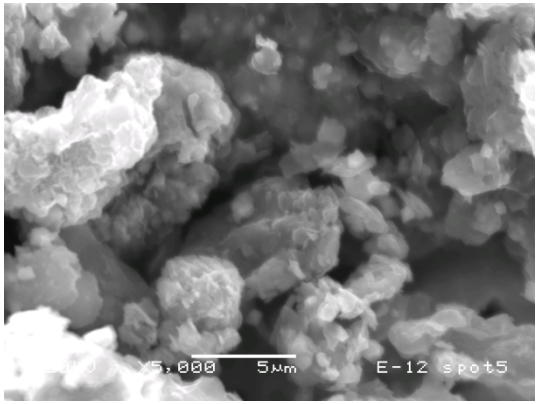
d: ML3-2, 7/7/07



e: ML3-2, 3/3/09



f: ESC-12, 4.6-4.8 m, 3/19/09



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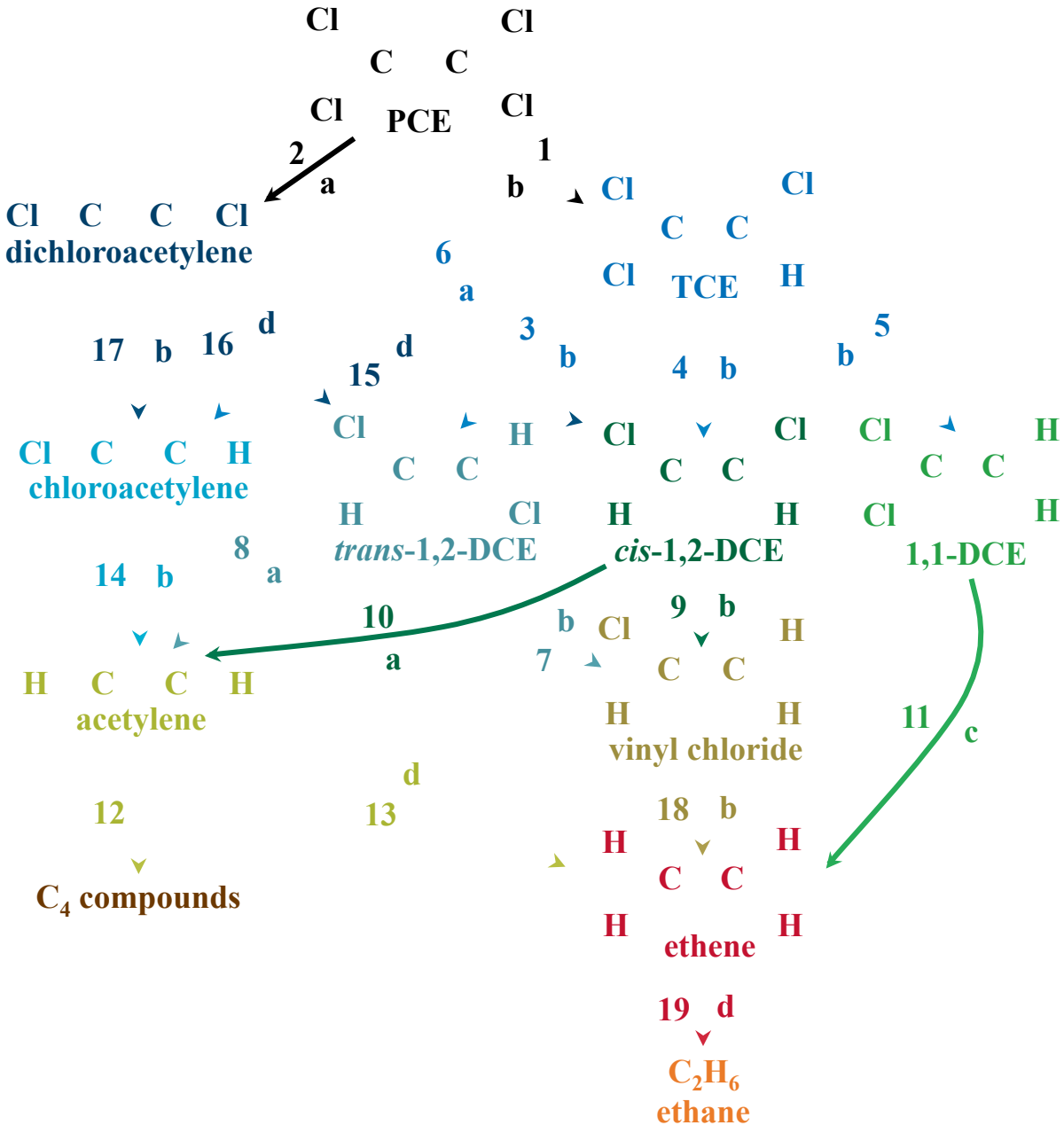
Degradation Pathways

a: β-elimination
b: Hydrogenolysis
c: α-elimination
d: Hydrogenation



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Conclusions

- Injected nanoiron was transformed to iron oxides (with greater particle size) mostly within three months.
- EZVI resulted in more reducing conditions that stimulated dechlorinating bacteria; there is no evidence of adverse effect to the microbial communities.
- Radius of influence was as much as 2.1 m with pneumatic injection and 0.89 m with direct injection.
- There were significant reductions in the downgradient groundwater mass flux.
- There were significant reduction in total VOC and DNAPL.
- EZVI technology can be successfully applied to treat source zone DNAPL.

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Questions?


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