EMULSIFIED ZERO-VALENT IRON TREATMENT OF CHLORINATED SOLVENT DNAPL SOURCE AREAS

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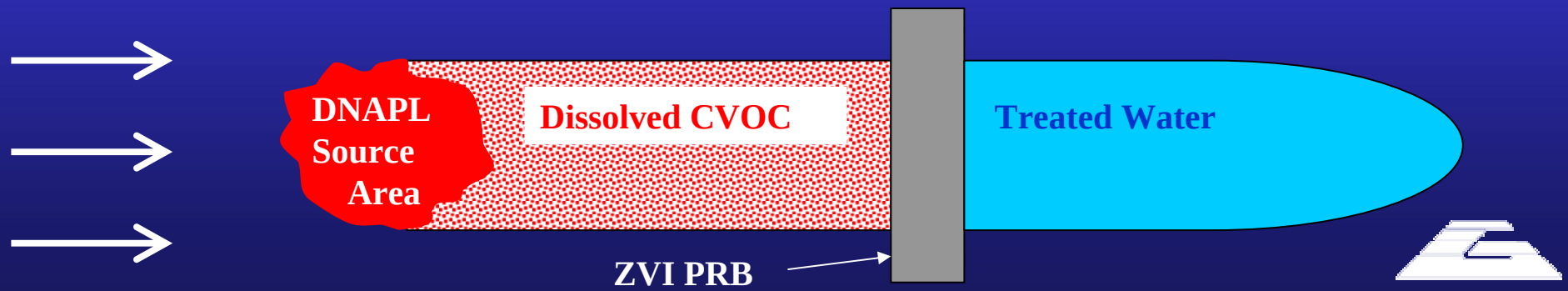
Outline

- Technology Rationale
- Properties of EZVI
- EZVI Technology Demonstration
- EZVI Injection Testing
- On-Going Work

Technology Rationale

- ZVI is an accepted technology for degradation of dissolved CVOCs such as PCE and TCE to ethene.

- 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.



Technology Rationale

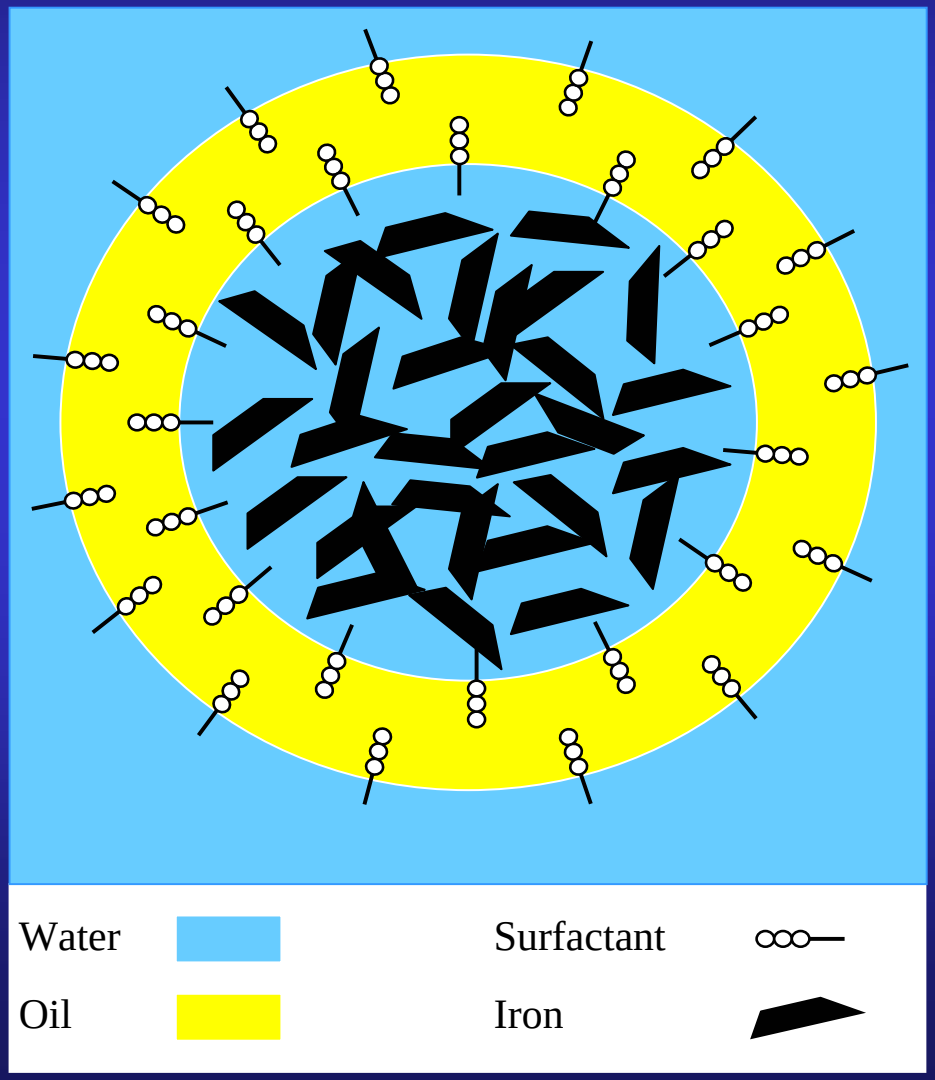
- ZVI needs to be in the presence of water to promote reductive dehalogenation → injection of ZVI into a DNAPL source zone will only treat the dissolved phase at the edges of the DNAPL.

- EZVI can be used to enhance degradation of DNAPLs by enhancing contact between the DNAPL and the ZVI particles.

Technology Development

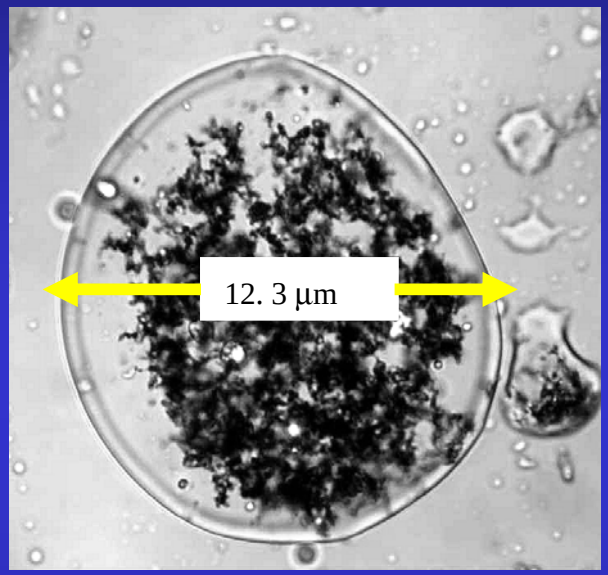
- Emulsified Zero-Valent Iron (EZVI) was developed at the UCF with funding from NASA's STTR program
- NASA holds the patent for EZVI
- GeoSyntec has a license for manufacturing and applying EZVI

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)

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 are degraded 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.

Properties of EZVI
In Contact with DNAPL

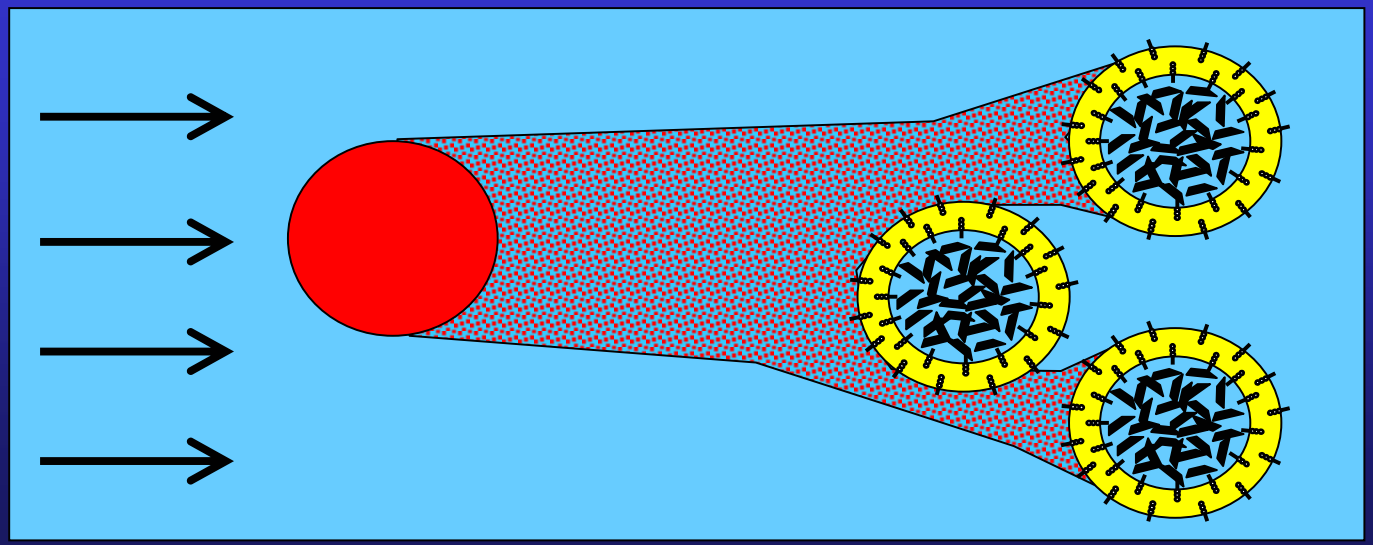
DNAPL
dyed red

DNAPL with micro-
scale ZVI

DNAPL with
EZVI

Properties of EZVI
In Contact with Dissolved Phase

- EZVI was developed to treat DNAPLs, however it will also treat dissolved phase components.
- Although design of injection method will be to maximize the contact between EZVI and DNAPL, any EZVI located near DNAPL will also degrade the dissolved-phase CVOCs, enhancing mass dissolution from the DNAPL.



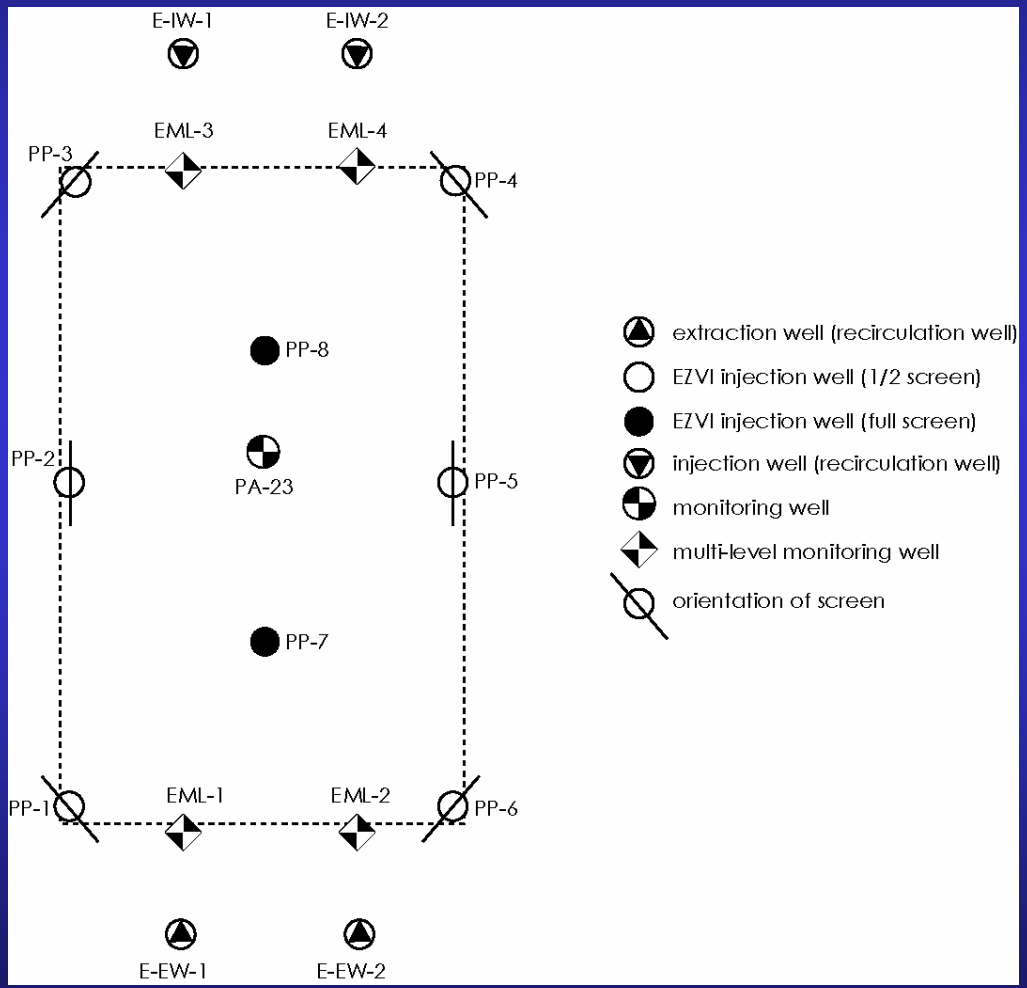
EZVI Technology Evaluation
Demonstration at LC34

- Demonstration conducted at NASA LC34.
- Pilot test area (PTA) 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:
  - GW (5 depth intervals, 2 upgradient and 2 downgradient wells); and
  - soil cores (8 depth intervals, 6 locations).

EZVI Technology Evaluation
Demonstration at LC34

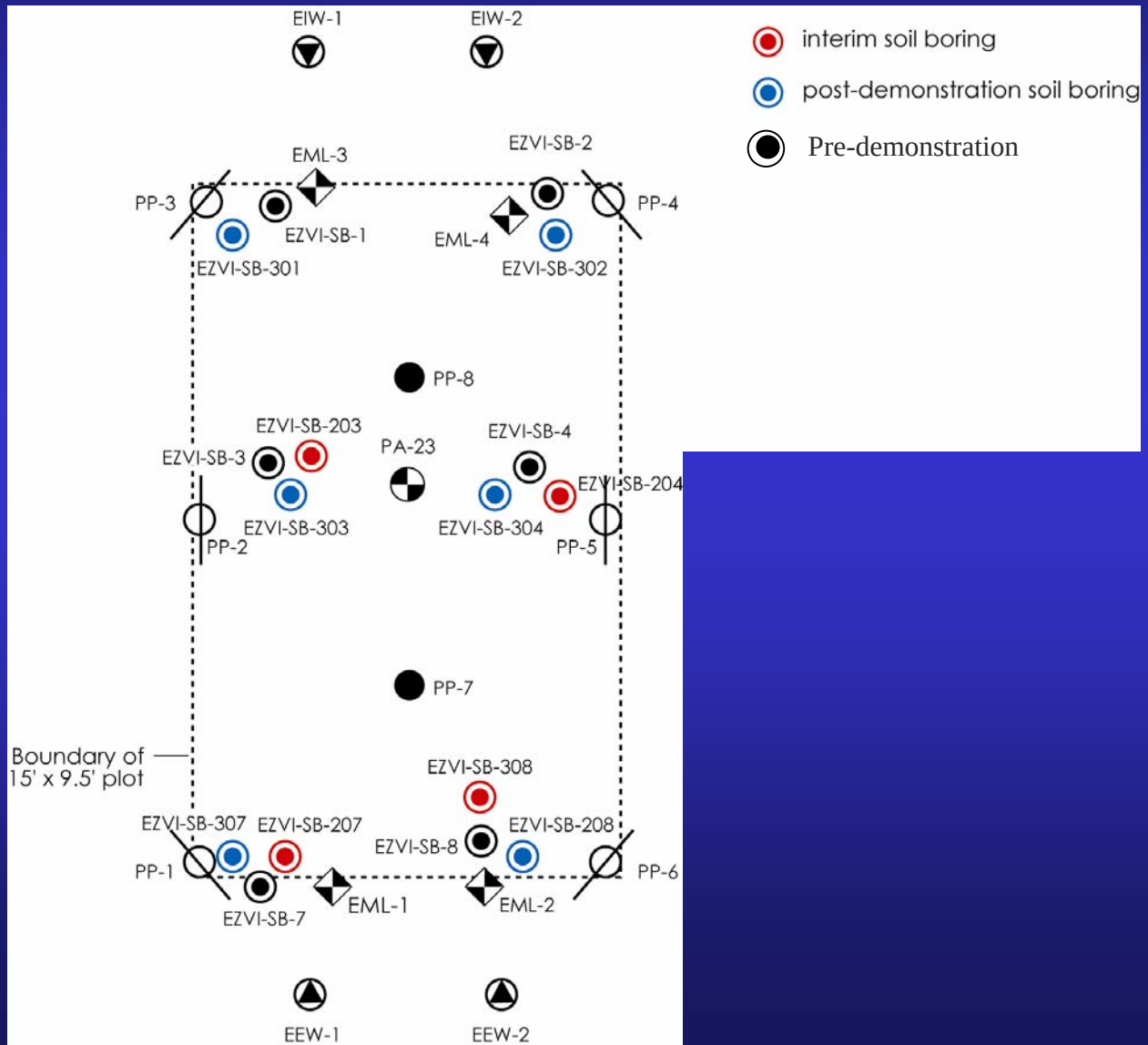
- Pressure Pulse Technology (PPT) chosen to inject the EZVI into the subsurface.
  - applies large-amplitude pressure pulses to porous media causing “instantaneous” dilation of the pore throats in the porous media
  - increases fluid flow and minimizing the “fingering” effect that occurs when a fluid is injected into a saturated media

Monitoring and Injection Locations



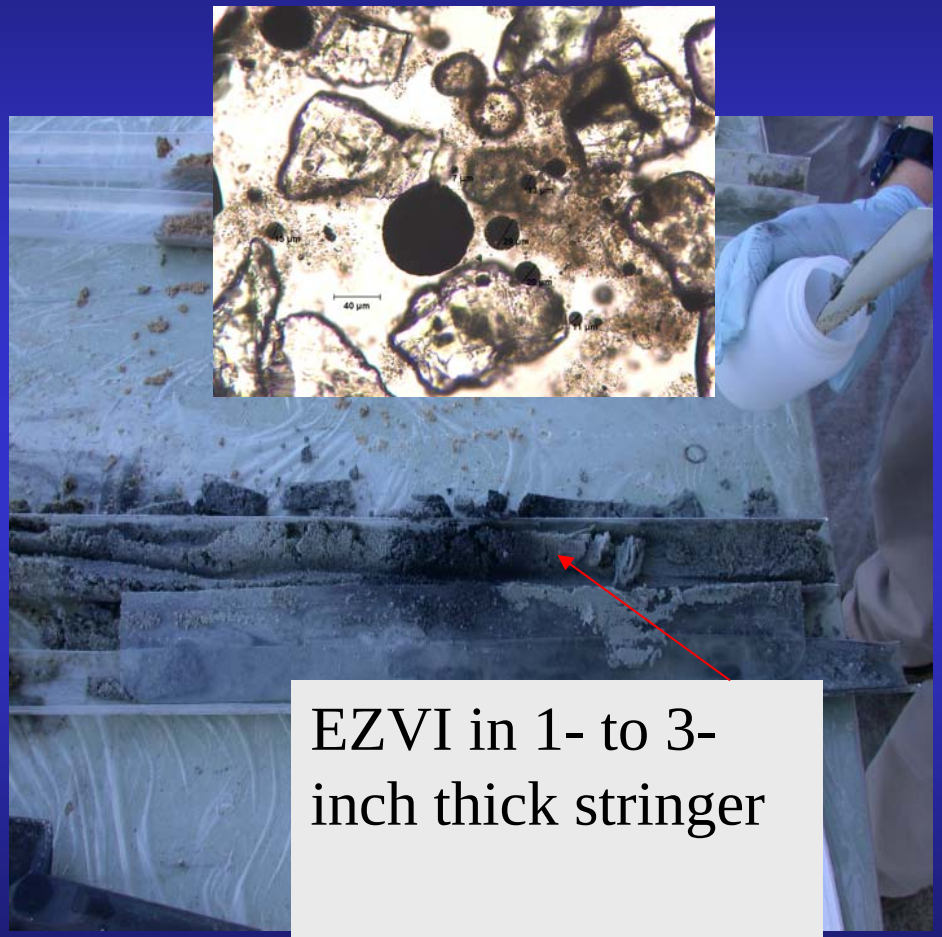
- EZVI injected in 8 injection wells
- Injection wells along edge of plot directed inwards
- Injection wells in center were fully screened
- Injection at 2 discrete depth intervals in each well

Pre-, Interim and Post-Demonstration Soil Cores



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



Results of Demo at LC34

		SB-1		SB-3		
Top Depth (ft)	Bottom Depth (ft)	Pre-Demo SB-1	Post-Demo SB-301	Pre-Demo SB-3	SB-203	Post-Demo SB-303
6	8	ND	0	ND	1	0
8	10	1	1	0	NA	0
10	12	1	1	0	1	1
12	14	3	4	1	1	1
14	16	6	1	7	13	4
16	18	87	1	6,067	1	1
18	20	282	12	209	1,023	451
20	22	208	8	195	798	7
22	24	230	0	253	495	4,502
24	26	283	NA	272	2	17
26	28	263	119	252	1	45

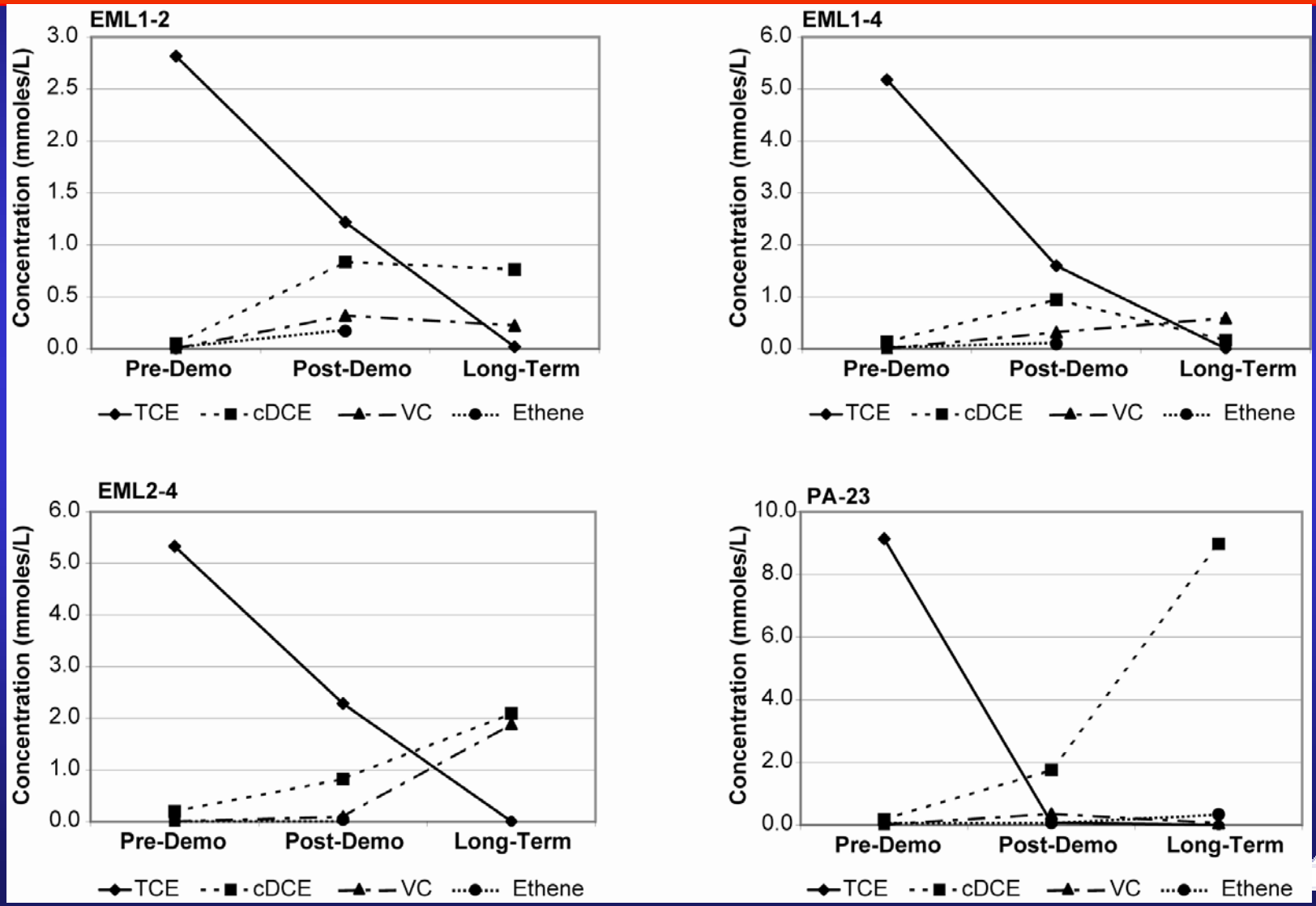
Results of Demo at LC34

		SB-7			SB-8		
Top Depth	Bottom Depth	Pre-Demo SB-7	SB-207	Post-Demo SB-307	Pre-Demo SB-8	SB-208	Post-Demo SB-308
6	8	ND	1	0	ND	ND	ND
8	10	0	NA	NA	3	ND	0
10	12	0	1	2	2	ND	1
12	14	2	ND	1	2	ND	0
14	16	70	ND	0	21	ND	NA
16	18	1,167	0	NA	127	ND	0
18	20	207	54	23	136	ND	NA
20	22	175	ND	NA	157	NA	177
22	24	202	268	19	162	143	130
24	26	222	177	149	212	NA	125
26	28	268	252	175	237	269	NA
28	30	249	248	NA	226	NA	248

Results of Demo at LC34

- 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 ongoing
  - Elevated cis-1,2-DCE, VC suggest biodegradation due to oil as an electron donor may also be significant

Results of Demo at LC34



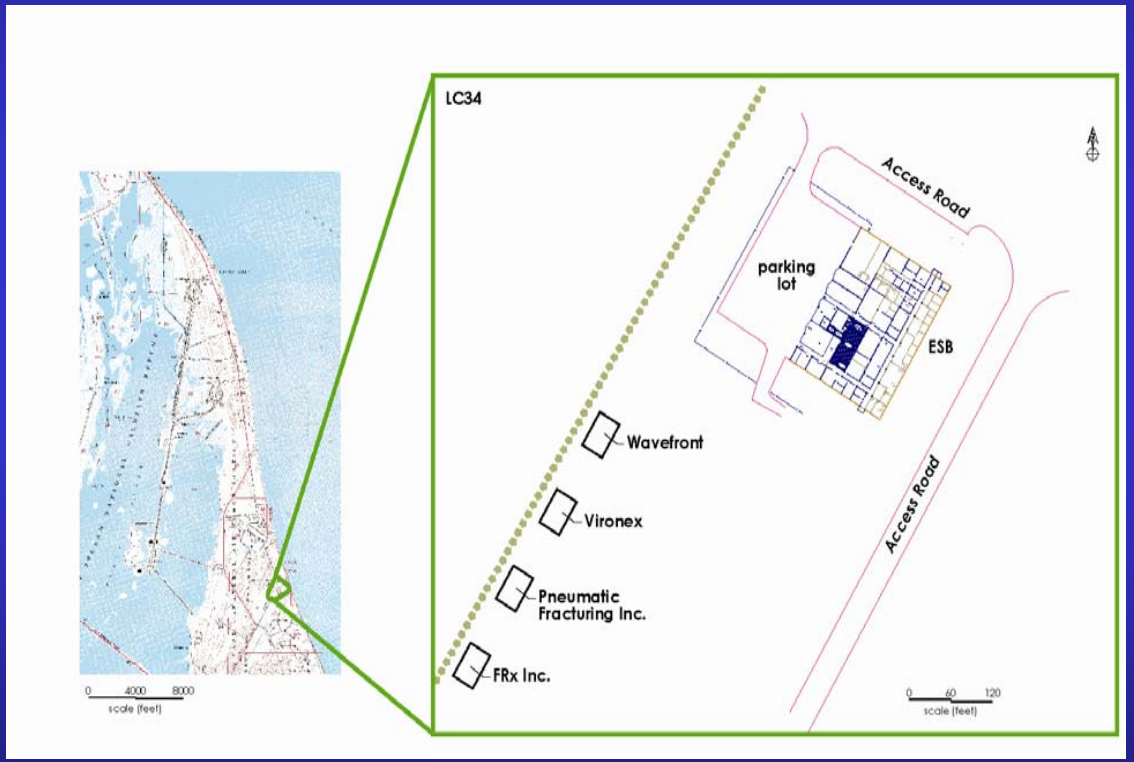
Recommendations From LC34 Demonstration

- 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

- Evaluation of four different injection techniques to improve ability to deliver EZVI to source zone.

Injection Techniques Field-tested at LC34

- January 2004 a series of injection tests conducted at LC34 using:
  - Pressure Pulsing
  - Pneumatic Fracturing
  - Hydraulic Fracturing
  - Direct Injection



Field Injection Test Objectives

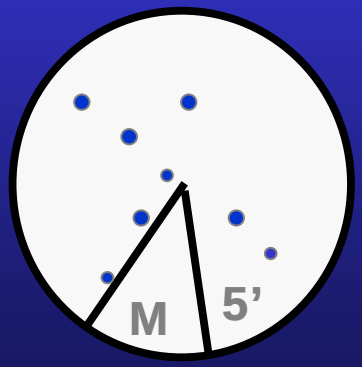
- **Each vendor 100 gallons of EZVI containing nanoscale iron**
- **Inject at depths between 16 and 19 ft bgs depending on how the injection technique**
- **Vendors were to attempt to distribute over a narrow and controlled injection interval and achieve maximum ROI.**
- **Immediately following injection, soil cores and FLUTe® liners were used to evaluate where and how far the EZVI was distributed**

Pneumatic Injection

- **Vendor: Pneumatic Fracturing Inc.**
- **Utilized nitrogen for pneumatic fracturing/fluidization and as carrier fluid**
- **2 step injection procedure**
  - **formation was first fluidized followed by EZVI injection**
- **Bullet-shaped nozzle that can rotate, allowing for 360-degree injection capability**

Pneumatic Injection Results

- **No evidence of emulsion damage (i.e., shearing of emulsion droplets) during injection**
- **EZVI distribution in subsurface visually confirmed at target depth**
- **Achieved 270-degree injection pattern at a ROI of 4 ft …believed that could have pushed further given larger volume of EZVI**
- **Single injection thickness of 6-8 inches**



Hydraulic Fracturing

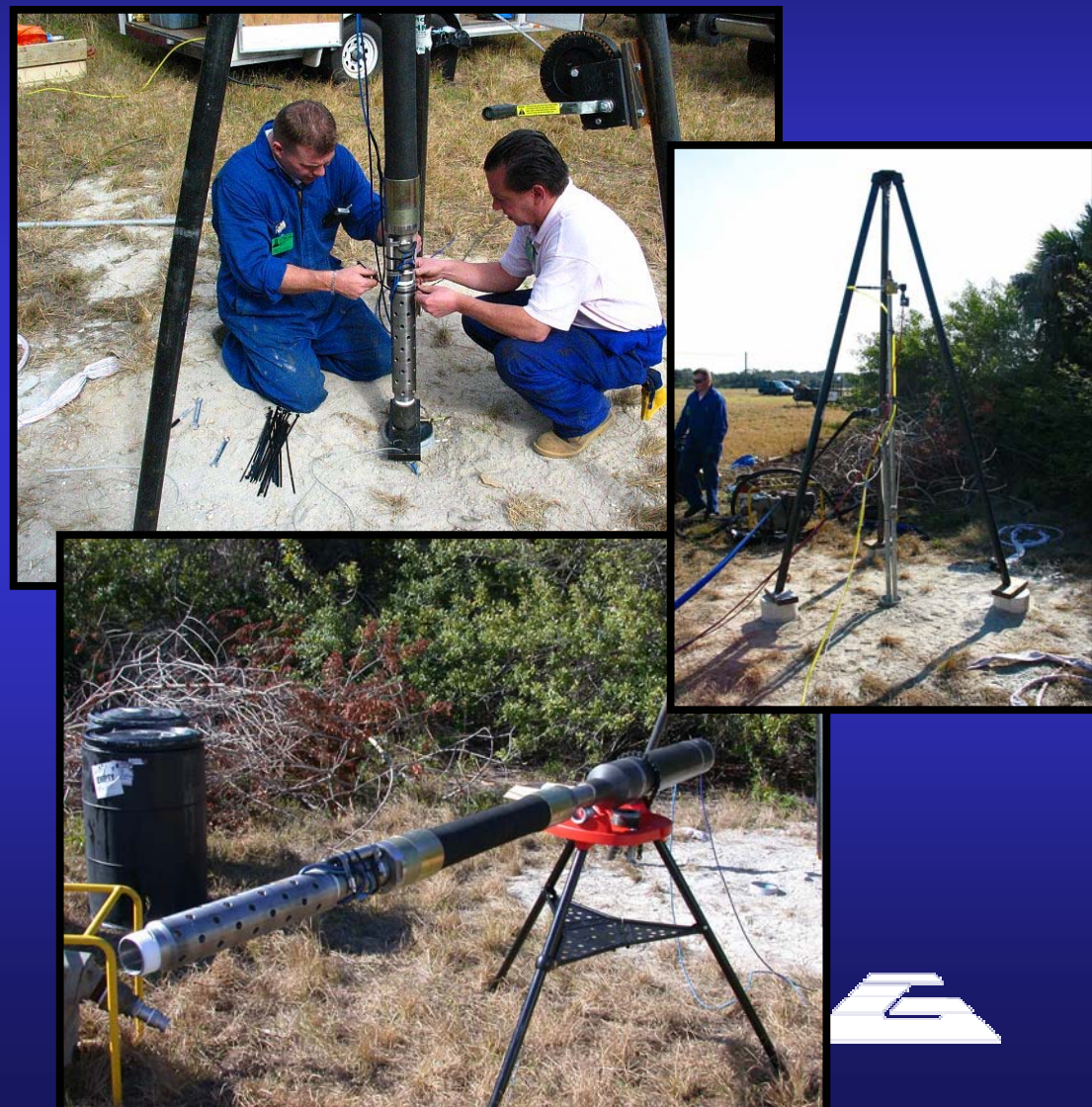
- **Vendor: FRx, Inc.**
- **Inject through a GeoProbe® rod fitted with a drive point**
- **Cut a thin notch in the wall of the borehole using a horizontal hydraulic jet**
- **Pressurized the notch with guar gel to initiate horizontal fracture and followed with EZVI to propagate the fracture**

Hydraulic Fracturing Results

- **Process of creating a hydraulic fracture in unconsolidated sediments….”A BIG IF” to start with**
- **Most important data point gained: No damage to the EZVI was noted in the sample**
- **No EZVI was detected on either of two FLUTe® liners installed at a 5’ ROI**
- **Five soil cores were collected at the injection location**
- **Only one sample showed a small lens of the EZVI at 2’ from the injection port**

Pressure Pulse Injection

- **Vendor: Wavefront Technologies, Inc.**
- **Injecting fluid while simultaneously applying large-amplitude pressure pulses**
- **Vendor planned an alternating water and EZVI injection with a 10:1 ratio of water to EZVI**
- **Target EZVI injection depth of 15-16’ bgs**



Pressure Pulsing

- **EZVI was found in soil cores at near the injection well at 8 to 16 ft bgs – well above target injection depth**
- **Evidence suggests the EZVI found a path of least resistance and was not dispersed omni-directionally outwards**
- **When EZVI encountered the flute liner, short-circuit to surface**
- **Still evidence of upward movement of EZVI although EZVI is well dispersed in sediments**

Direct Injection

- Vendor: Vironex, Inc.
- Injected using two different direct injection techniques, one of which utilized an ultrasound transducer
- Injected 50 gallons per test at two different locations and depth intervals
- Utilized water as a carrier fluid

Direct Injection Results

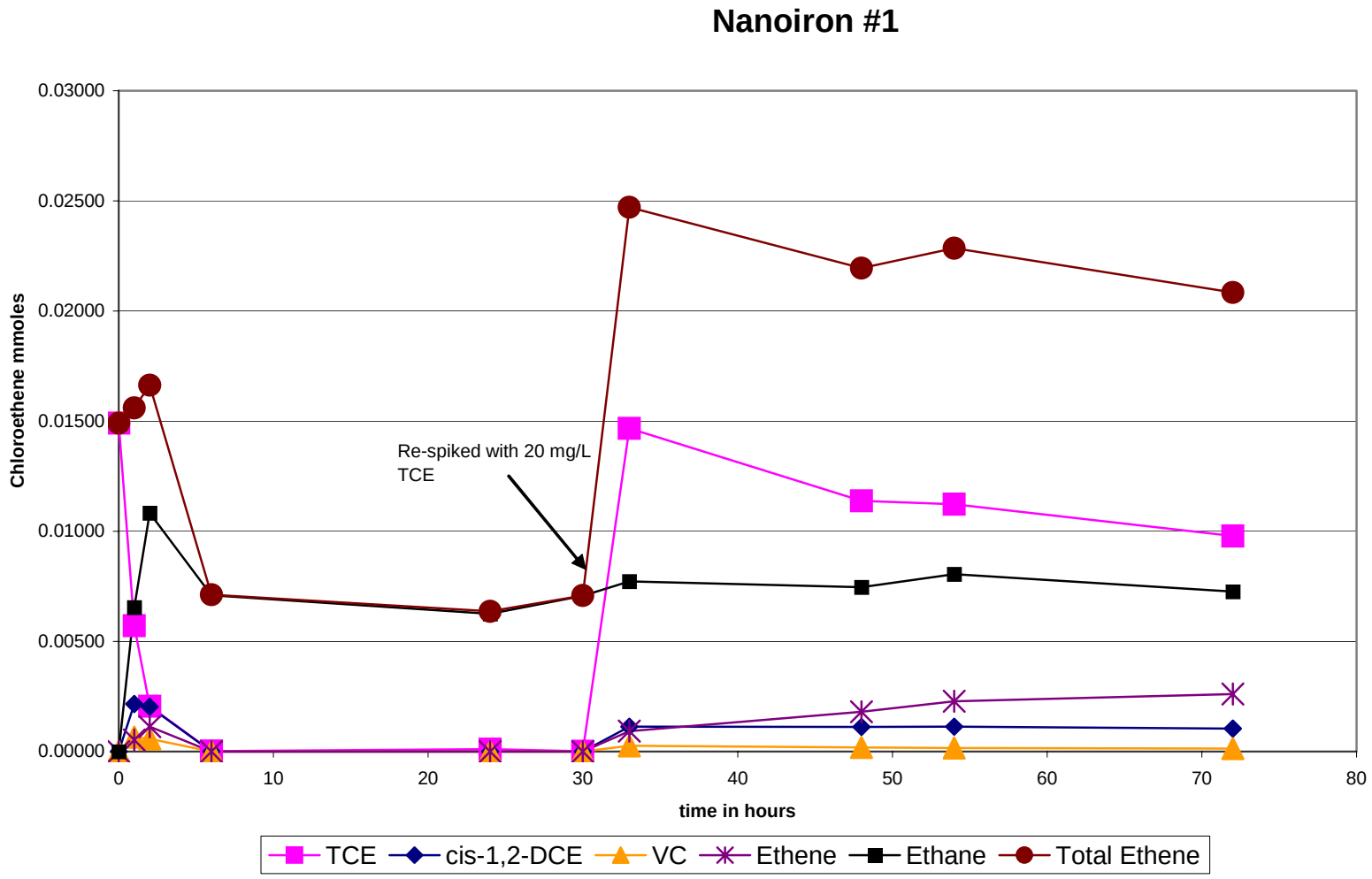
- **Direct injection inadvertently sited over a cemented sand layer**
- **Repeated efforts to collect soil cores after injection were not successful. Broke numerous rods attempting to collect samples**
- **Previous results conducted without ultrasound at LC34 (6/2003) indicated that direct injection with Vironex's rig is capable of installing a column of EZVI with a ROI of 0.75 ft. at the target depth**
- **No evidence of short-circuiting with Vironex rig**

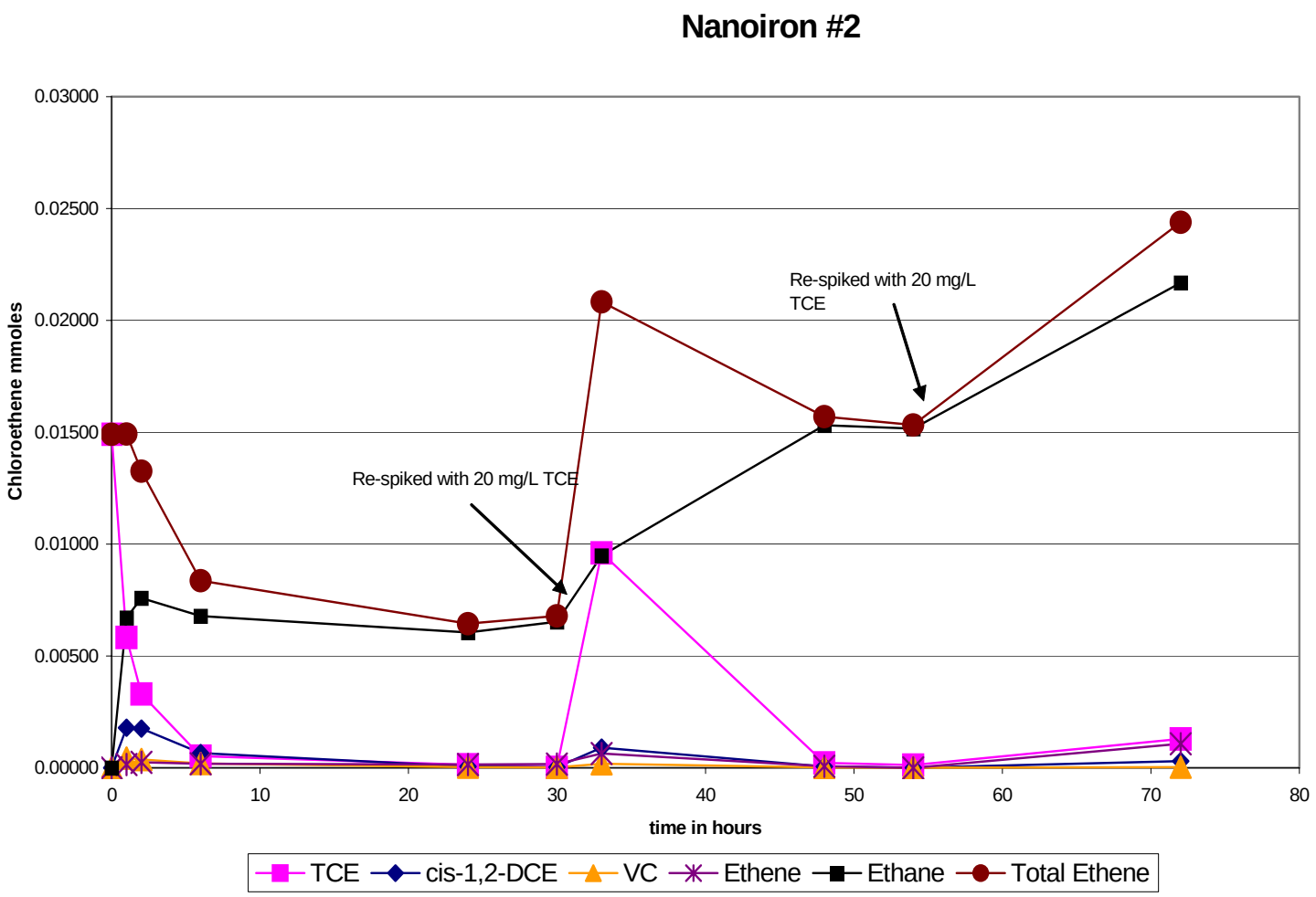
Ongoing Work
ESTCP Pilot Test Demonstration

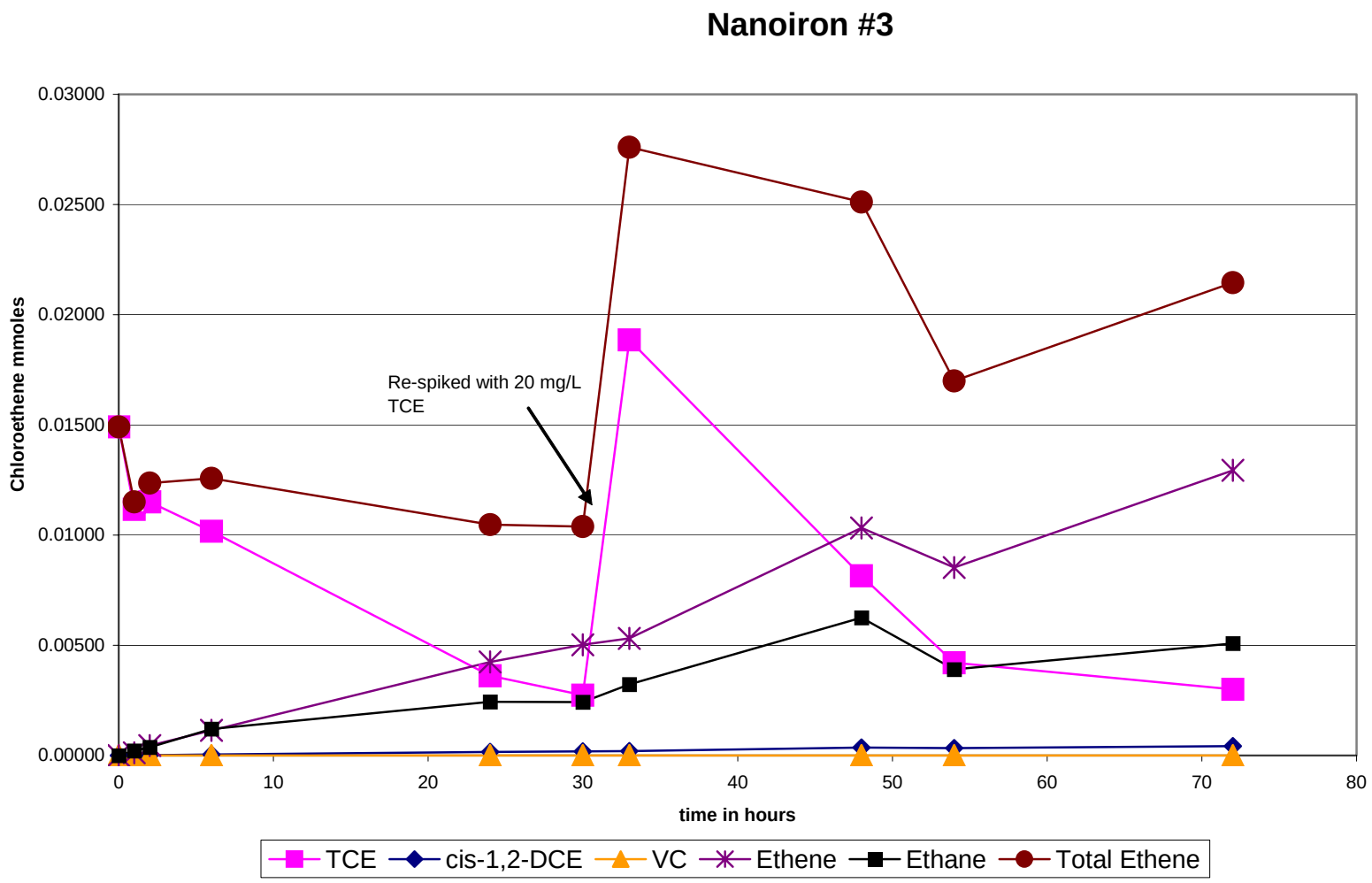
- Pilot-scale demonstration of EZVI funded by the DOD ESTCP – GeoSyntec, NASA and US Navy collaboration
- More research on determining % of degradation due to ZVI and % due to biodegradation
- EZVI deployment in two pilot test areas within a DNAPL source zone using the two most promising EZVI injection technologies with the objective of providing cost and performance data.

Treatability Testing

- Series of treatability test bottles
  - controls
  - EZVI, TCE spiked groundwater, KB-1
  - EZVI components minus the ZVI, TCE spiked groundwater, KB-1
  - ZVI, TCE spiked groundwater, KB-1
- Treatability tests done in triplicate and each test set up is done in both sterile and non-sterilized set ups
- Activity Assays to Evaluate different nanoscale iron products
  - Toda America RNIP
  - OnMaterials Zloy (with and without dispersant)
  - Others?


Nanoiron #1
Chloroethene mmoles
0.03000
0.02500
0.02000
0.01500
0.01000
0.00500
0.00000
0
10
20
30
40
50
60
70
80
time in hours
Re-spiked with 20 mg/L TCE
TCE
cis-1,2-DCE
VC
Ethene
Ethane
Total Ethene


Nanoiron #2
0.03000
0.02500
0.02000
0.01500
0.01000
0.00500
0.00000
Chloroethene mmoles
0
10
20
30
40
50
60
70
80
time in hours
Re-spiked with 20 mg/L TCE
Re-spiked with 20 mg/L TCE
TCE
cis-1,2-DCE
VC
Ethene
Ethane
Total Ethene


Nanoiron #3
Chloroethene mmoles
0.03000
0.02500
0.02000
0.01500
0.01000
0.00500
0.00000
0
10
20
30
40
50
60
70
80
time in hours
Re-spiked with 20 mg/L TCE
TCE
cis-1,2-DCE
VC
Ethene
Ethane
Total Ethene