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

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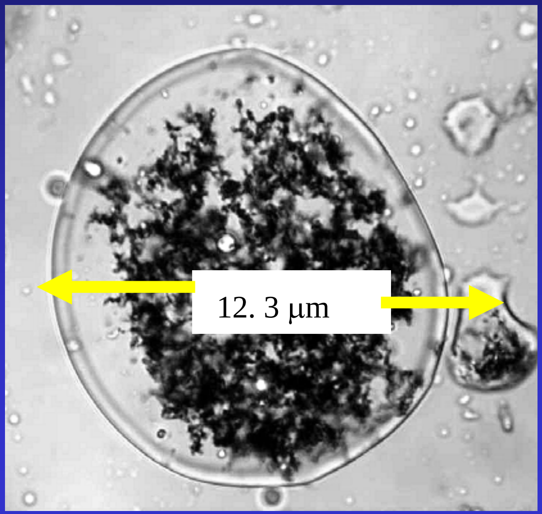
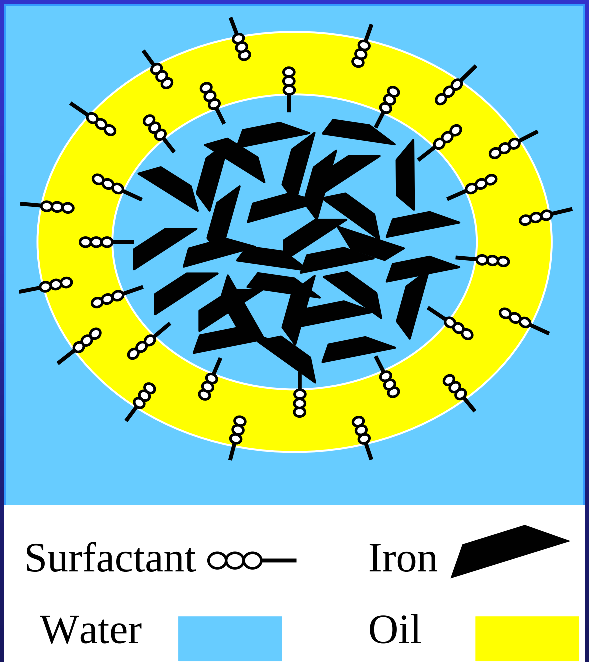
Technology Rationale

- ZVI is an accepted technology for the reductive dehalogenation 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.

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 undergo reductive dechlorination 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

EZVI Technology Evaluation
Demonstration at LC34

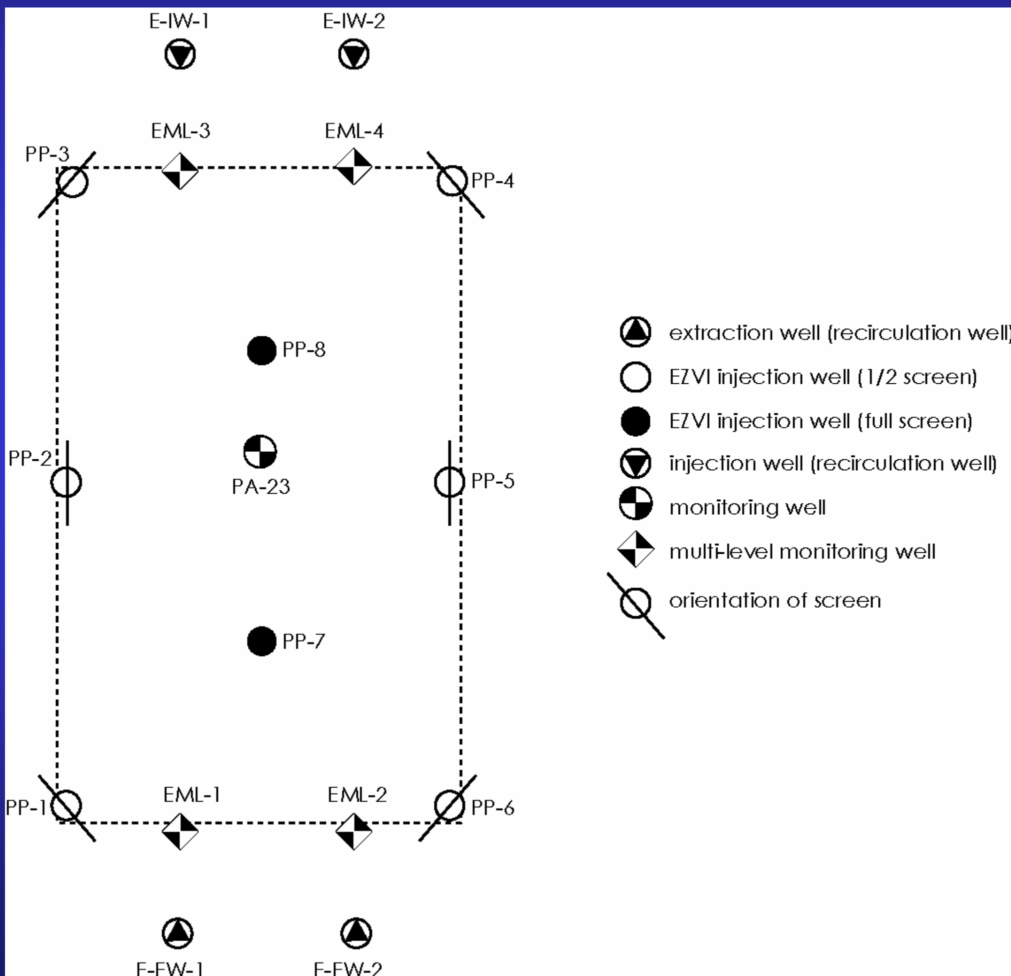
- Demonstration conducted at NASA LC34.

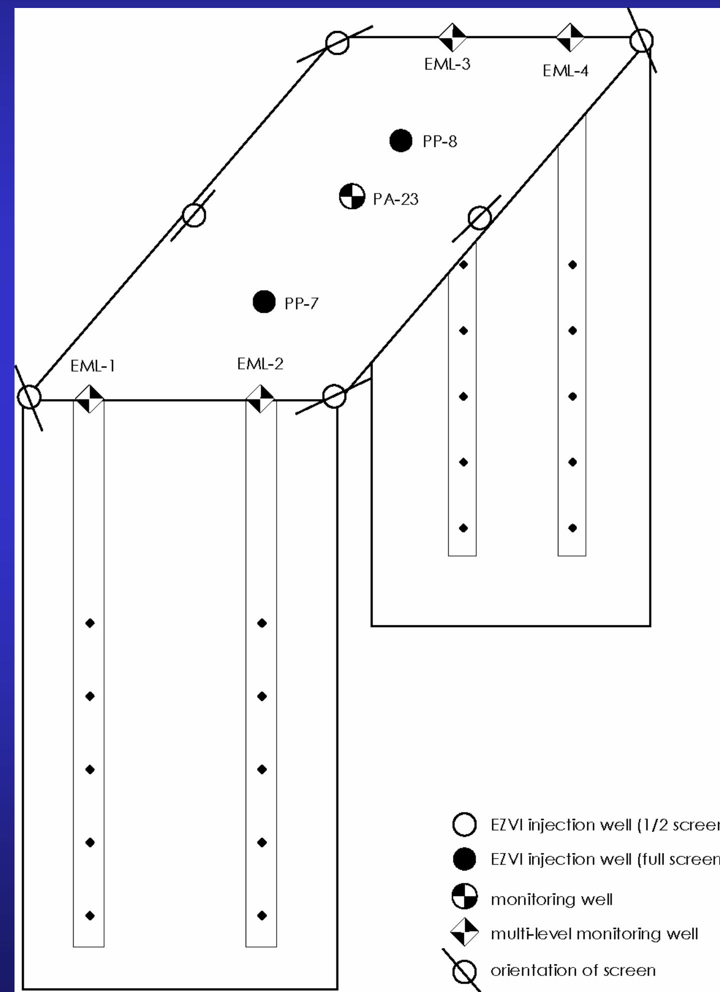
- Pilot test area (PTA) was inside of a building and was 15 ft by 10 ft.
  - hydraulically controlled for containment and to maintain consistent groundwater velocity in treatment zone.

- 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).

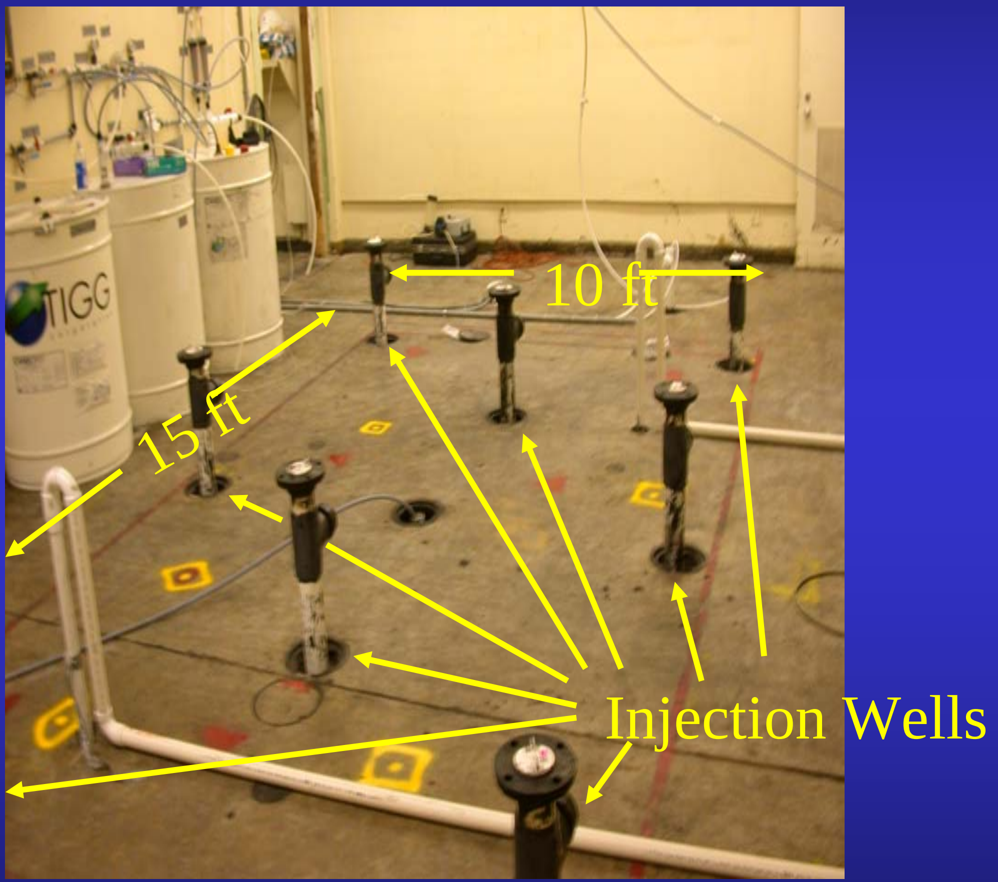
Monitoring and Injection Locations



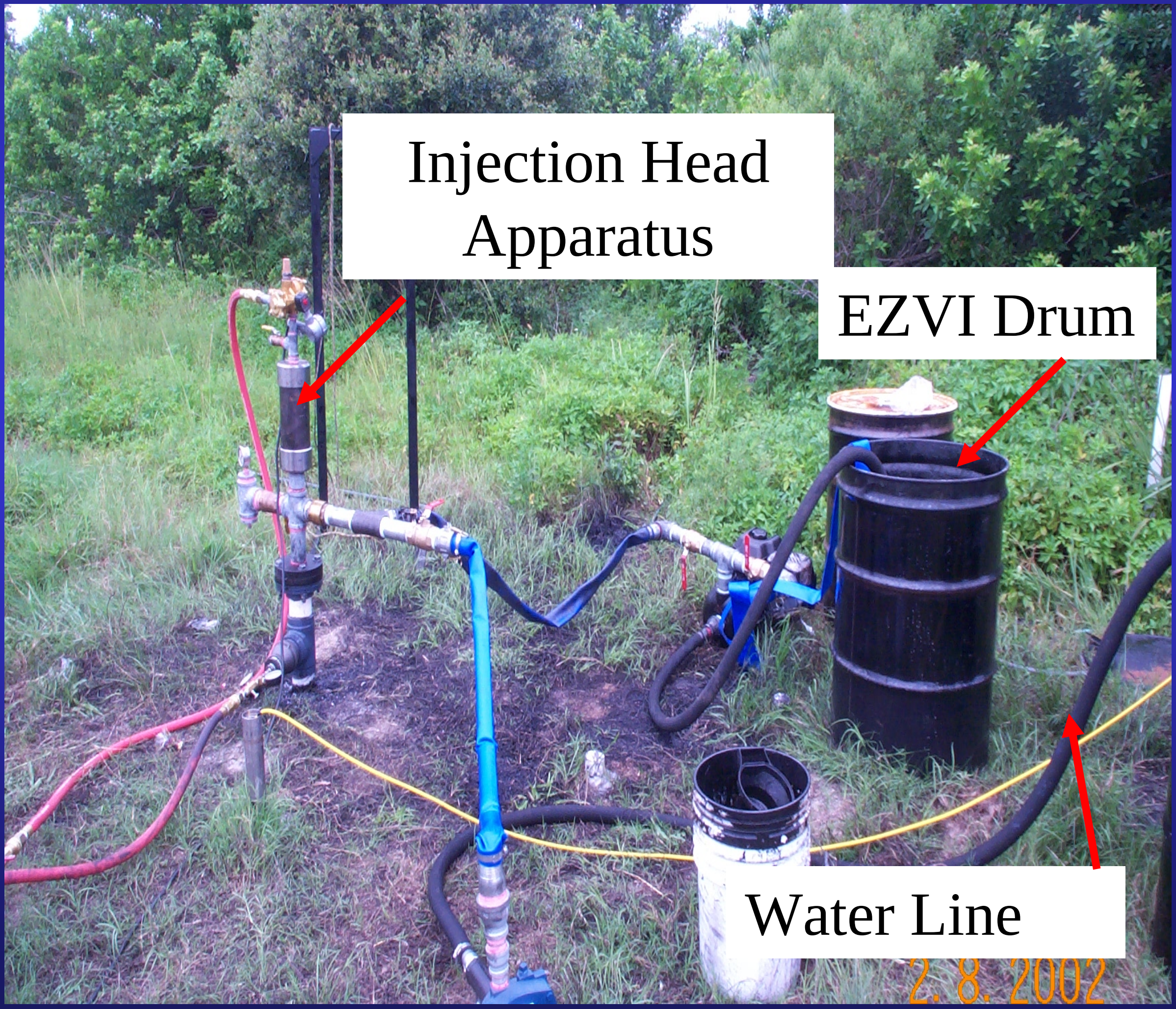


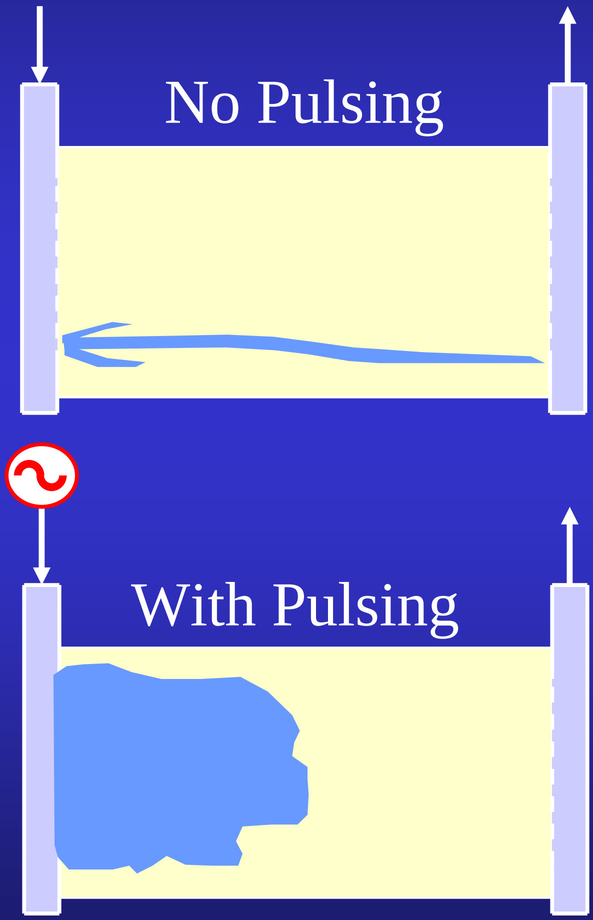
EZVI Injection Set-Up Within PTA

- 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



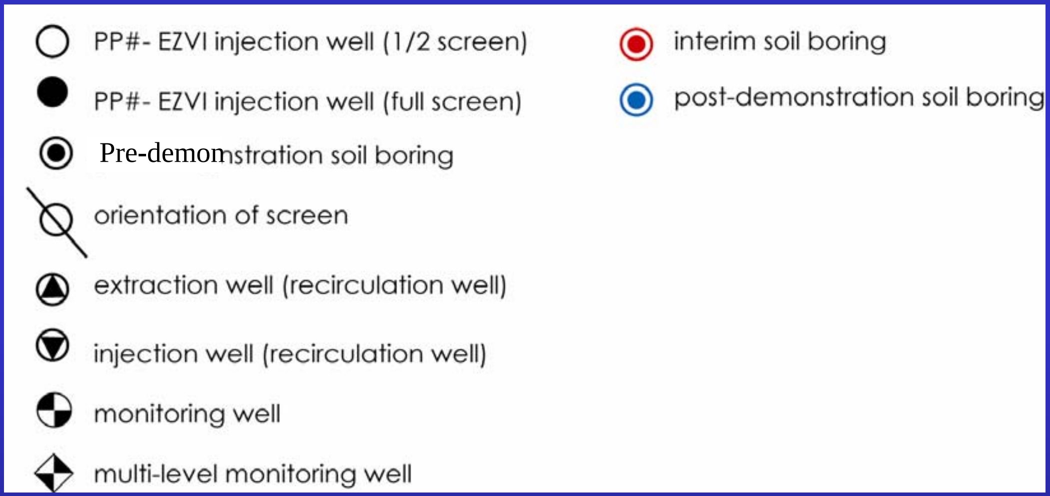
Pressure Pulse Technology

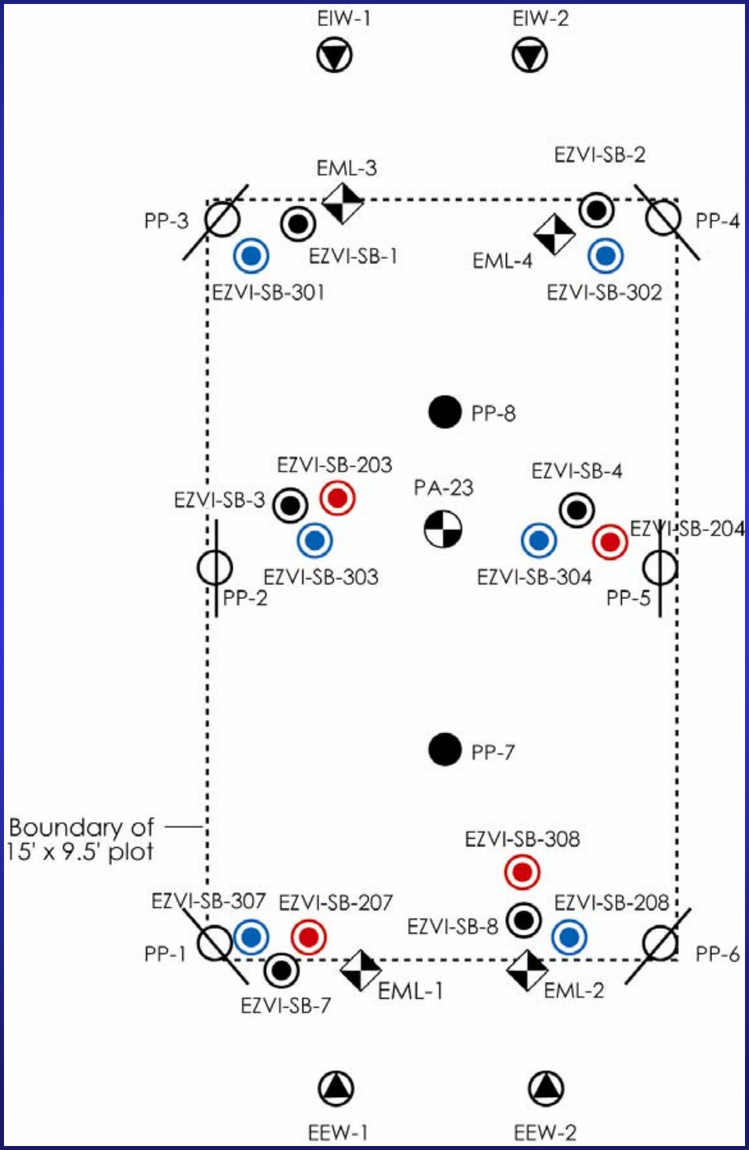




EZVI Injection Set-Up Within PTA

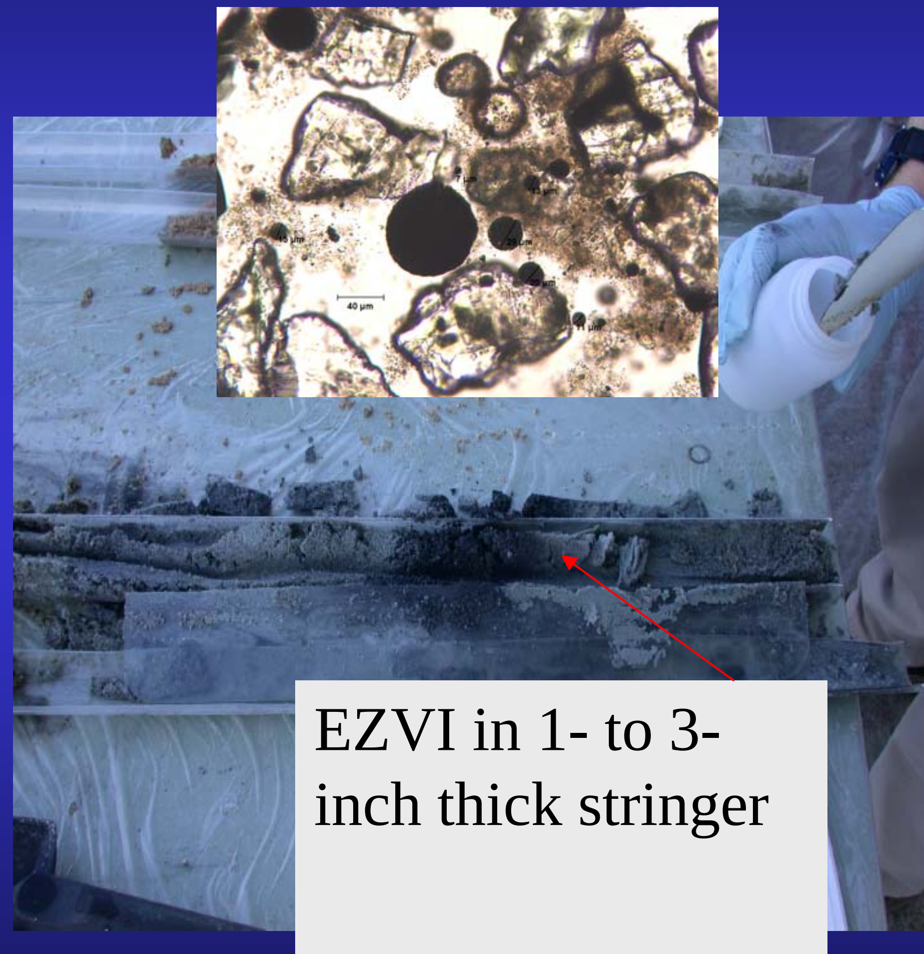
Pre and Post-Demonstration Cores





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

Top Depth (ft)	Bottom Depth (ft)	Pre-Demo SB-1	Post-Demo SB-301
6	8	ND	0
8	10	1	1
10	12	1	1
12	14	3	4
14	16	6	1
16	18	87	1
18	20	282	12
20	22	208	8
22	24	230	0
24	26	283	NA
26	28	263	119

SB-3

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

Results of Demo at LC34

Top Depth	Bottom Depth	SB-2 Pre-Demo SB-2	SB-2 Post-Demo SB-302	SB-4 Pre-Demo SB-4	SB-4 SB-204	SB-4 Post-Demo SB-304
6	8	ND	0	ND	ND	0
8	10	ND	NA	0	NA	0
10	12	ND	1	0	0	0
12	14	1	1	6	1	0
14	16	10	11	6	1	ND
16	18	89	5	45	1	ND
18	20	182	57	161	6	2
20	22	233	NA	171	3	1
22	24	262	18	249	35	0
24	26	259	7	289	183	0
26	28	270	8	255	27	28
28	30	196	144	236	133	193

Results of Demo at LC34

SB-7

Top Depth	Bottom Depth	Pre-Demo SB-7	SB-207	Post-Demo SB-307
6	8	ND	1	0
8	10	0	NA	NA
10	12	0	1	2
12	14	2	ND	1
14	16	70	ND	0
16	18	1,167	0	NA
18	20	207	54	23
20	22	175	ND	NA
22	24	202	268	19
24	26	222	177	149
26	28	268	252	175
28	30	249	248	NA

SB-8

Top Depth	Bottom Depth	Pre-Demo SB-8	SB-208	Post-Demo SB-308
6	8	ND	ND	ND
8	10	3	ND	0
10	12	2	ND	1
12	14	2	ND	0
14	16	21	ND	NA
16	18	127	ND	0
18	20	136	ND	NA
20	22	157	NA	177
22	24	162	143	130
24	26	212	NA	125
26	28	237	269	NA
28	30	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.
    - from 19.2 mmoles/ft^2/day down to 8.5 mmoles/ft^2/day
  - 18 months after injection groundwater concentrations indicate that long term degradation due to bioremediation ongoing

Results of Demo at LC34

- Elevated cis-1,2-DCE, VC suggest biodegradation due to oil as an electron donor may also be significant
- Bioaugmentation may enhance complete degradation associated with biological component of process

Injection Techniques Field-tested at LC34-2004

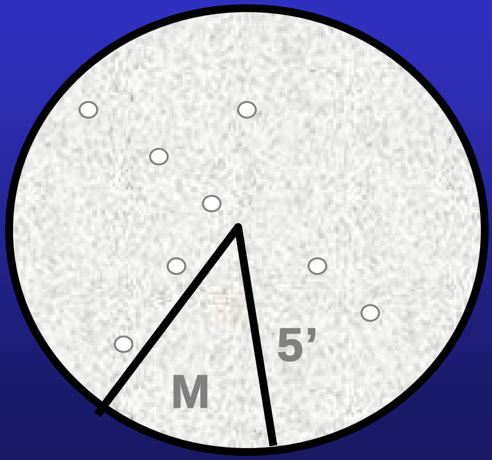
- Pressure Pulsing
- Pneumatic Fracturing
- Hydraulic Fracturing
- Direct Injection

Field Test Objectives:

- **Give each vendor 100 gallons of EZVI containing nanoscale iron.**
- **Inject at depths between 16 and 19 ft bls, depending on how the vendor intended to perform the test.**
- **Vendors should attempt to distribute over a narrow 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

Pneumatic Injection



M=missed interval

Blue dots=sample locations

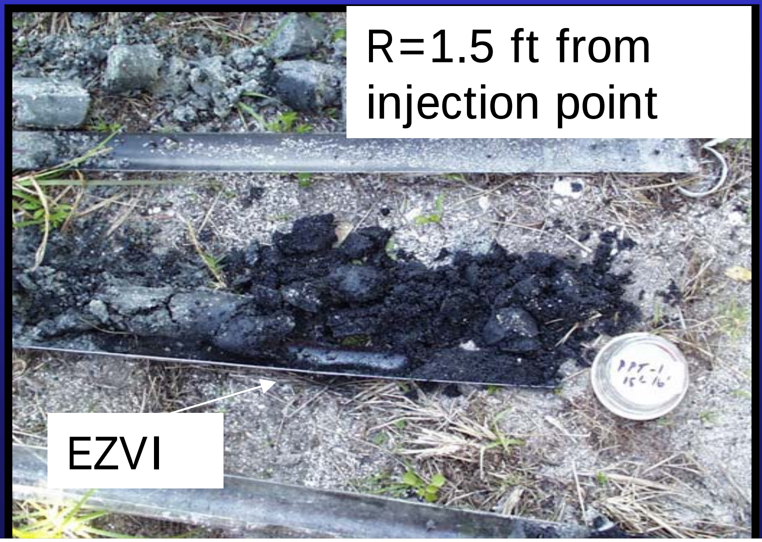
Hydraulic Fracturing

Hydraulic Fracturing

Pressure Pulsed Injection

Pressure Pulsing

Evidence suggests the EZVI found a path of least resistance somewhere between R=0.75 and R=1.5 feet and was not dispersed omni-directionally outwards.



Direct Push Injection

Conclusions:

- Pneumatic injection of EZVI in sandy soils looks promising. Able to disperse EZVI evenly and at target depths.

- Further testing using pneumatic injection concludes that micro-scale iron may be injected into sandy formations without emulsion deformation and a sufficient ROI is achievable. Saves $$$$

- Hydraulic fracturing of EZVI does not deform emulsion droplets. May have application in consolidated sediments or where tighter lithologies prevail.

Conclusions

- Pressure pulsing appears not to overcome soil heterogeneities enough for the highly viscous EZVI; approach may be suitable for aqueous-phase materials or pure vegetable oil.
- Direct push has application to small sites where a direct push rig can install a bunch of “columns” of EZVI in a single day, making it very cost competitive over injection technologies that seek larger ROIs.
- This is a NASA-patented Technology available for all US Government agencies to use royalty-free.

Upcoming Work
ESTCP Pilot Test Demonstration

- 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.