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

Suzanne O'Hara, Thomas Krug, GeoSyntec Consultants;

Cherie Geiger, Christopher Clausen, University of Central Florida;

Jacqueline Quinn, NASA; Sam Yoon, Battelle.

Outline

- Problem Statement
- Technology Rationale
- Properties of EZVI
- EZVI Technology Demonstration
- Summary of Pilot Test
- Results of Demonstration
- On-Going/Up-coming work

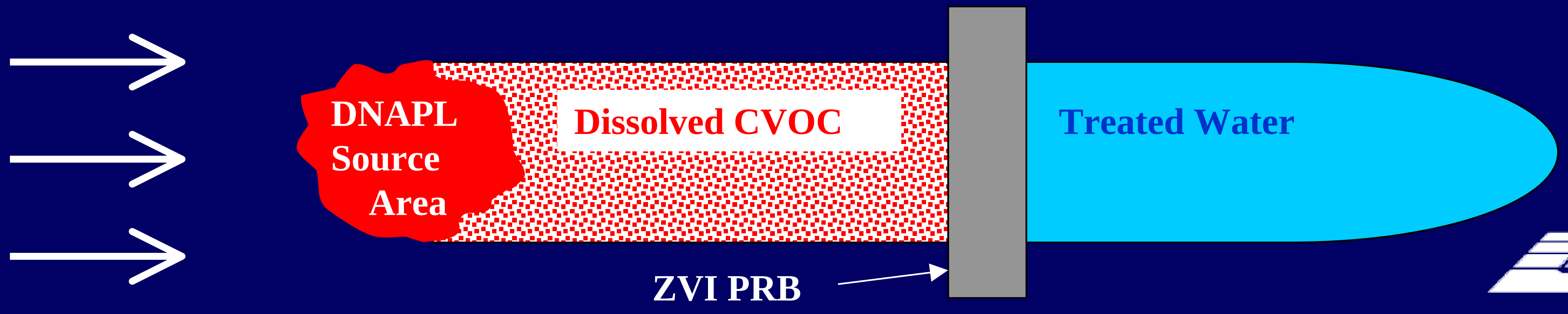
Problem Statement

- Chlorinated VOCs in groundwater at an overwhelming number of contaminated sites.
  - Significant portion of these sites have CVOCs present as DNAPLs.
- Slow dissolution of CVOCs from residual or pooled DNAPL source areas results in long operation periods and high costs for conventional remediation technologies.
- Source treatment technologies have potential to lower overall cost by reducing time required for remediation of DNAPLs.

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.



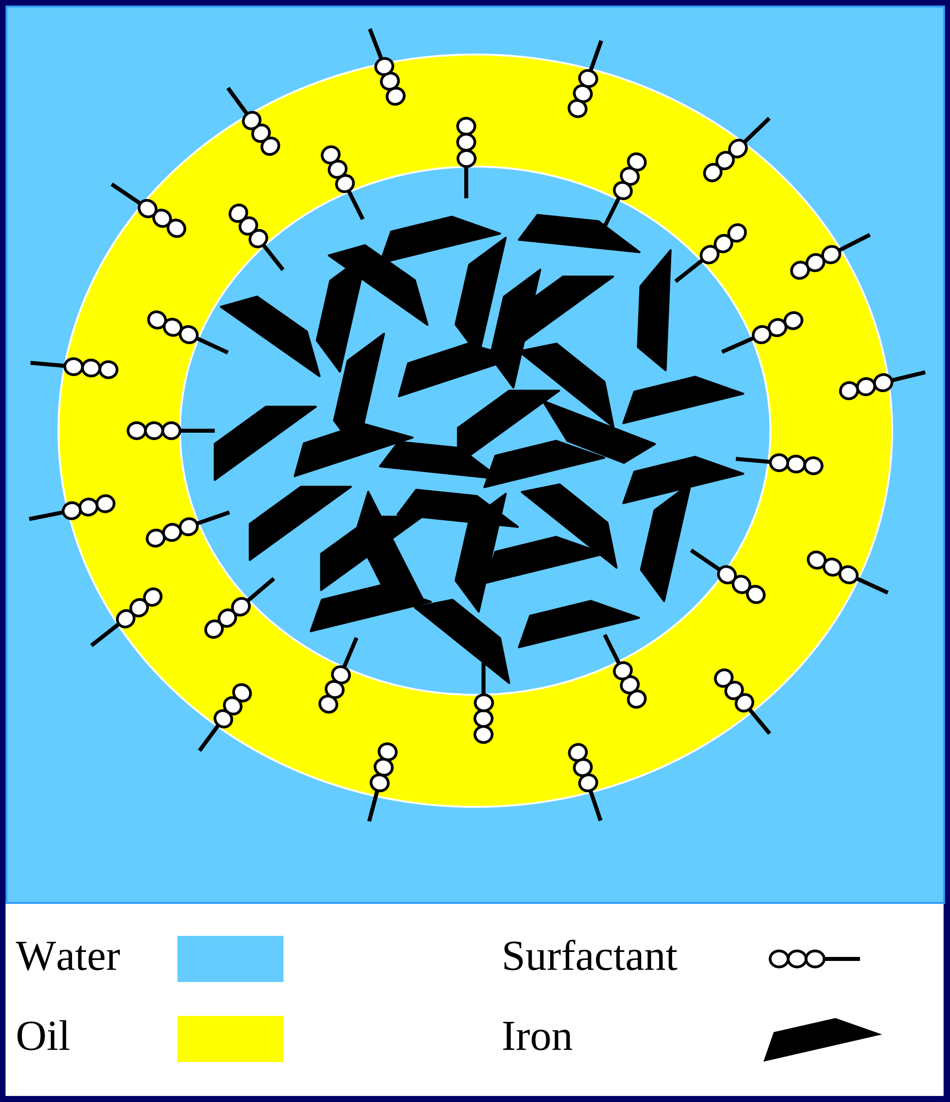
Technology Rationale

- 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 Rationale

- Emulsified Zero-Valent Iron (EZVI) was developed at the UCF with funding from NASA's STTR program
- NASA holds the patent for EZVI
- GeoSyntec, UCF and NASA have completed a field scale demonstration of the technology which was independently evaluated by Battelle as the US EPA's contractor for the SITE program
- GeoSyntec and NASA in the process of conducting a set of injection tests to evaluate different methods for the distribution of EZVI in subsurface

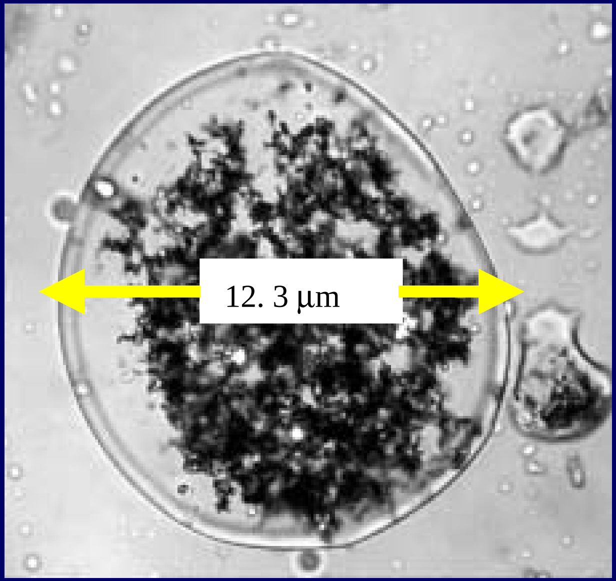
Properties of EZVI



- Emulsion droplets contain iron particles in water surrounded by an oil-liquid membrane

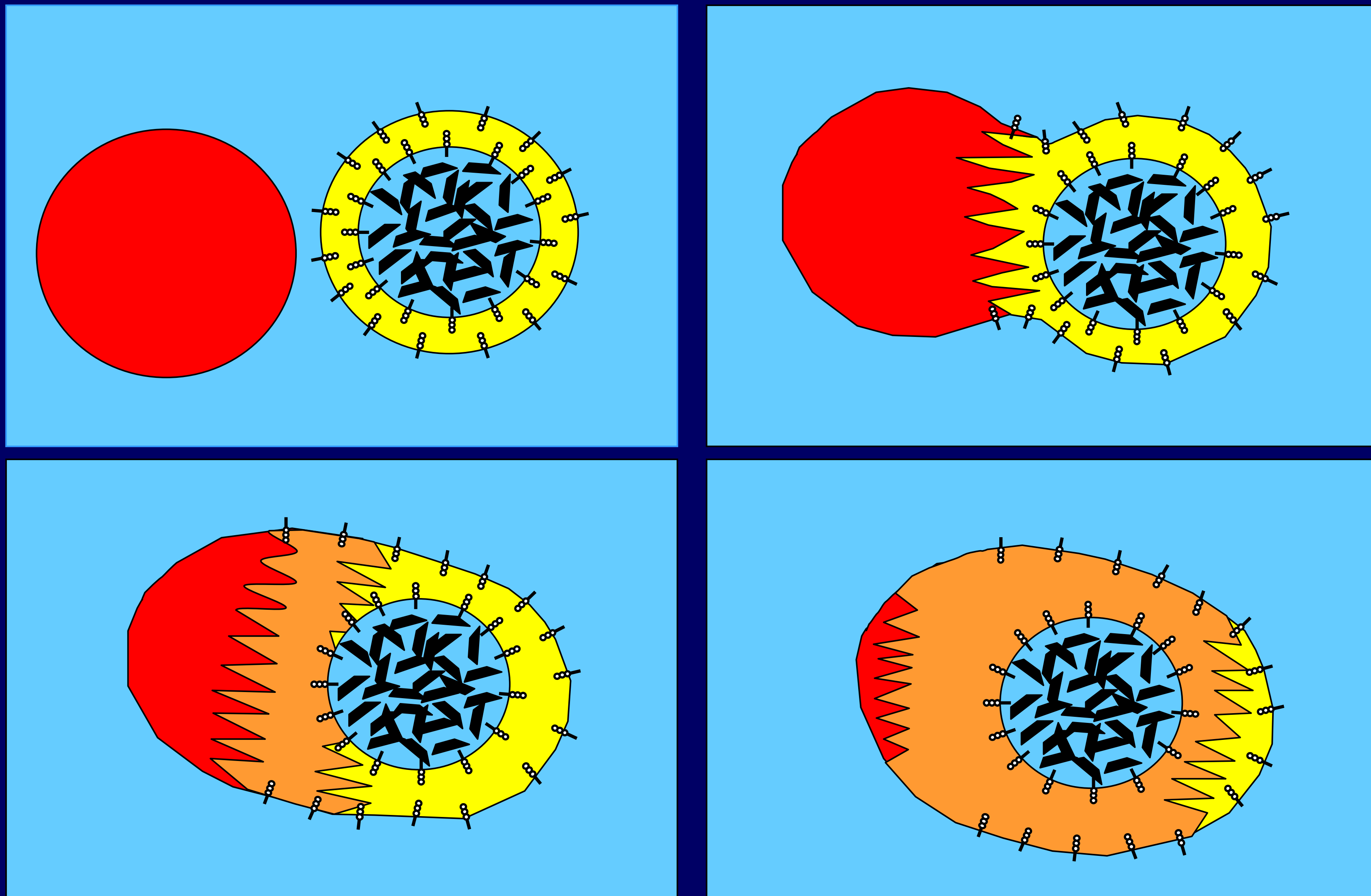
- EZVI composed of food-grade surfactant, biodegradable vegetable oil, water, and ZVI (nano- or micro-scale iron)

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 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



Properties of EZVI
In Contact with DNAPL

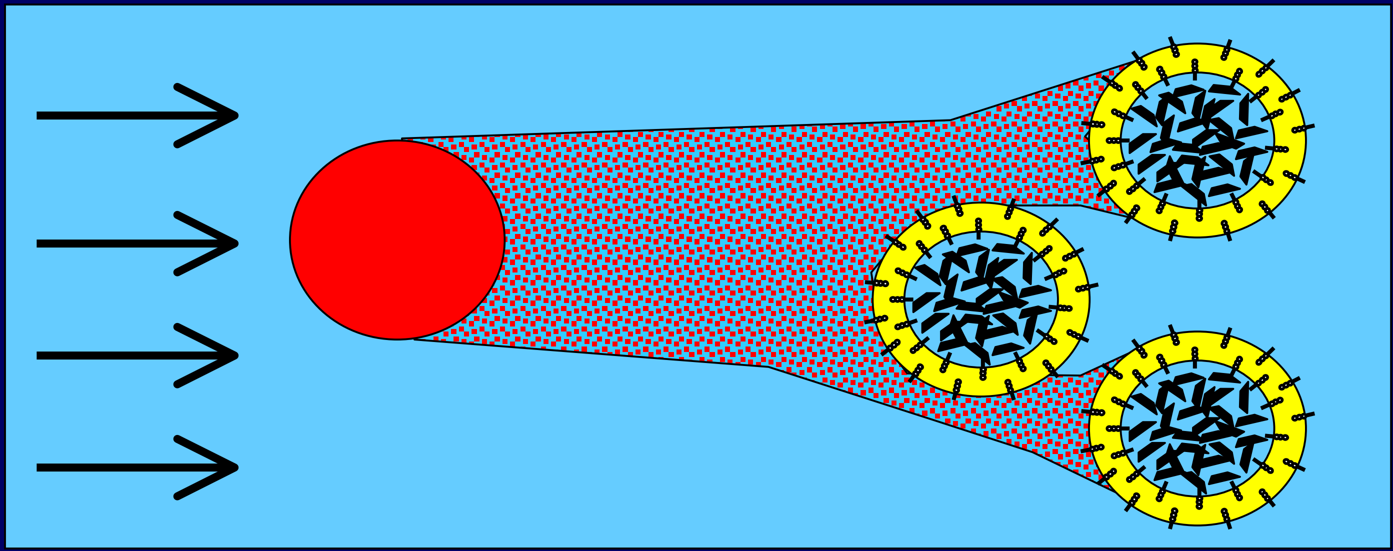
DNAPL
dyed red

DNAPL with micro-
scale ZVI

DNAPL with
EZVI

Properties of EZVI
In Contact with Dissolved Phase

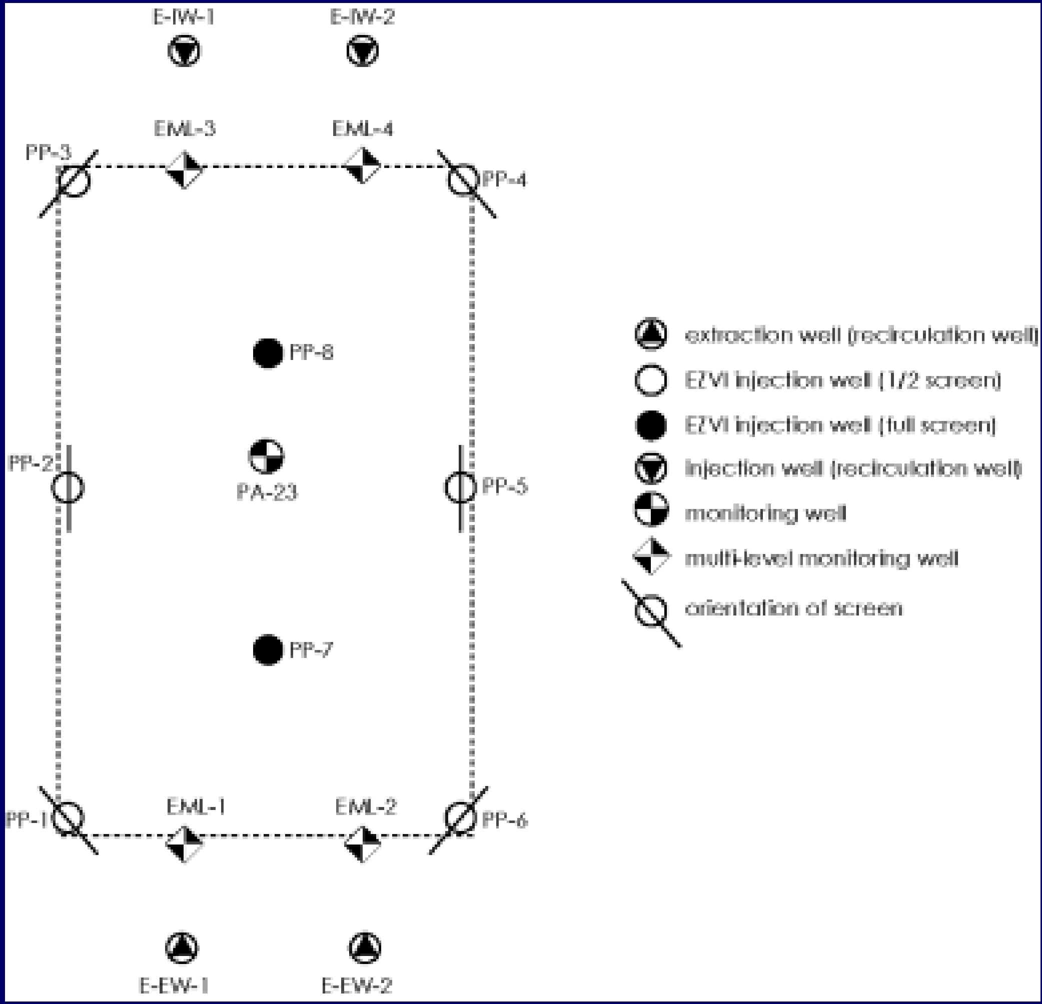
- EZVI was developed to treat DNAPLs, however it will also treat dissolved phase components.
- Although design of injection method will be to maximize the contact between EZVI and DNAPL, any EZVI located near DNAPL will also degrade the dissolved-phase CVOCs, enhancing mass dissolution from the DNAPL.



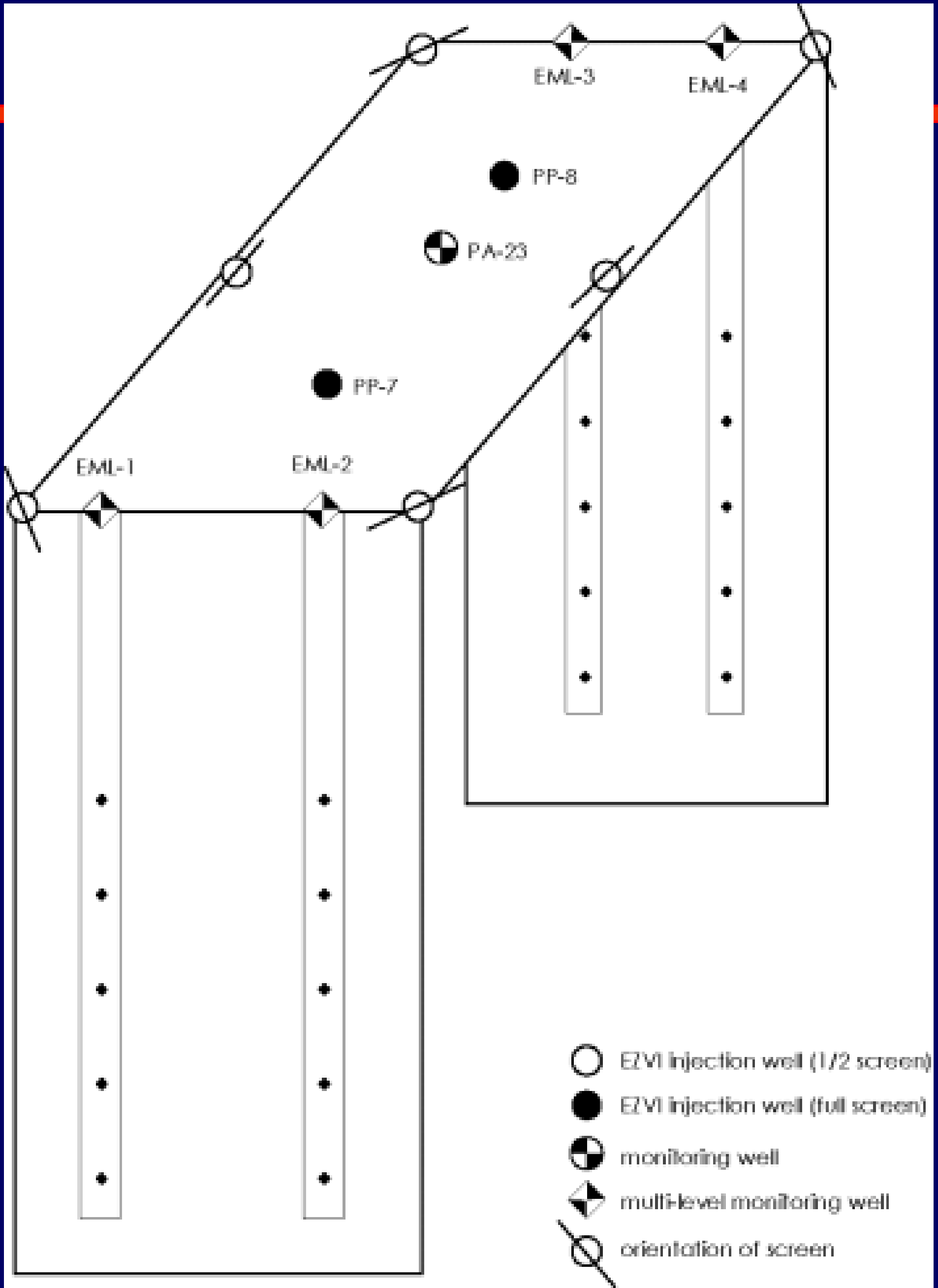
EZVI Technology Evaluation
Demonstration at LC34

- Demonstration conducted at NASA LC34.
- Pilot test area (PTA) was inside of a building and was 15 ft by 10 ft.
  - 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

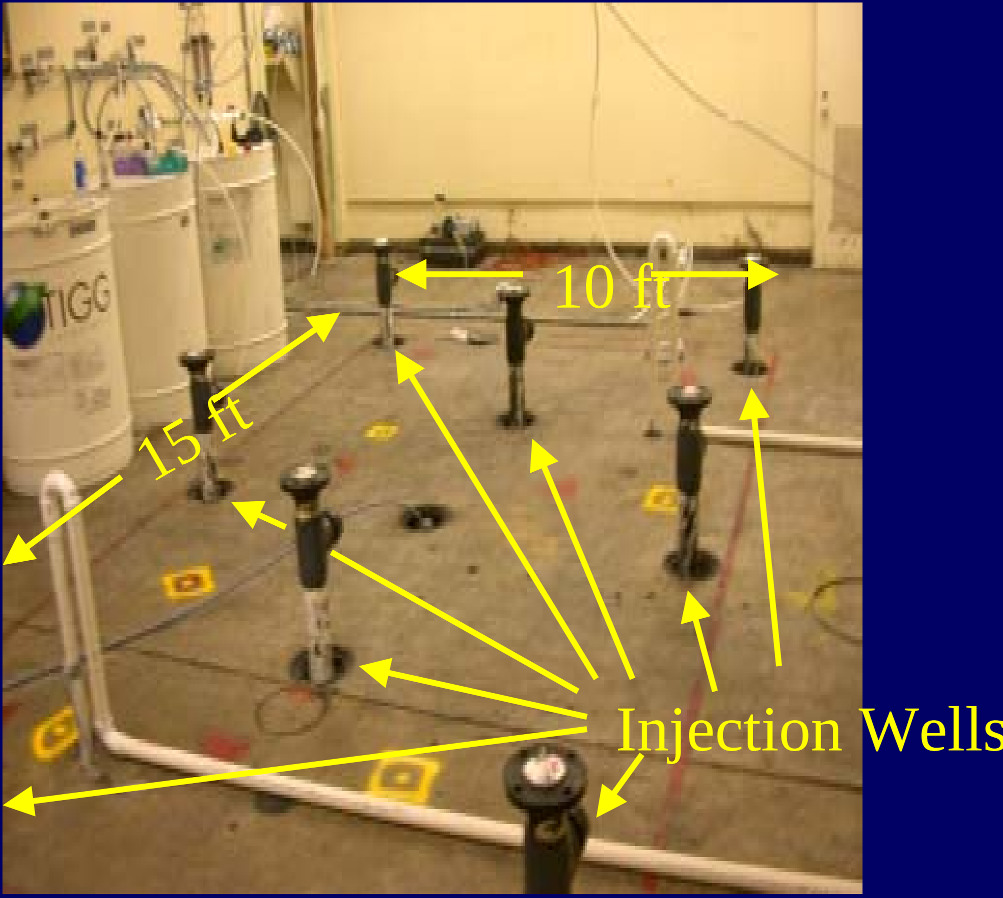


Monitoring and Injection Locations

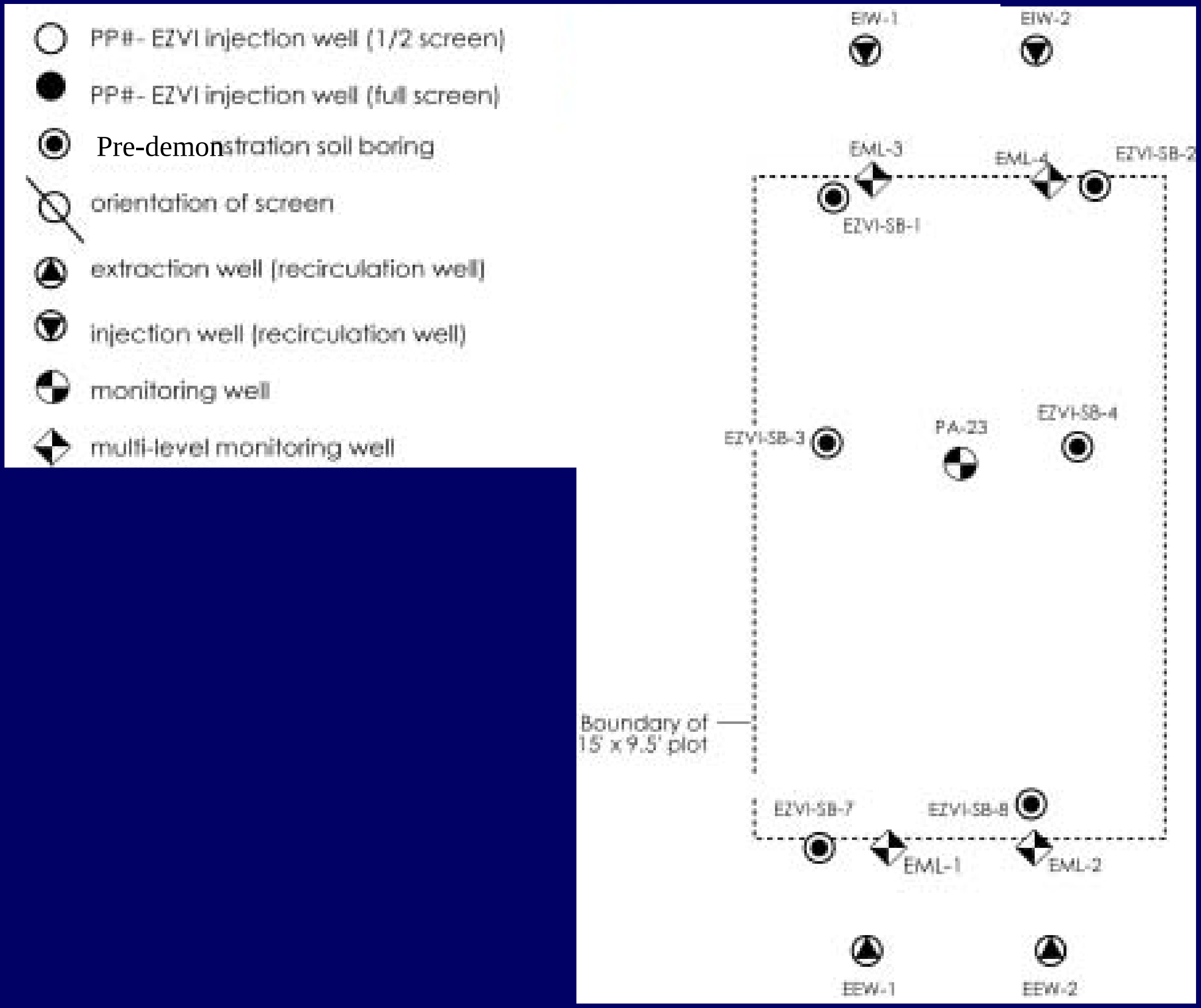


EZVI Injection Set-Up Within PTA

- 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



Pre-Demonstration Core Locations



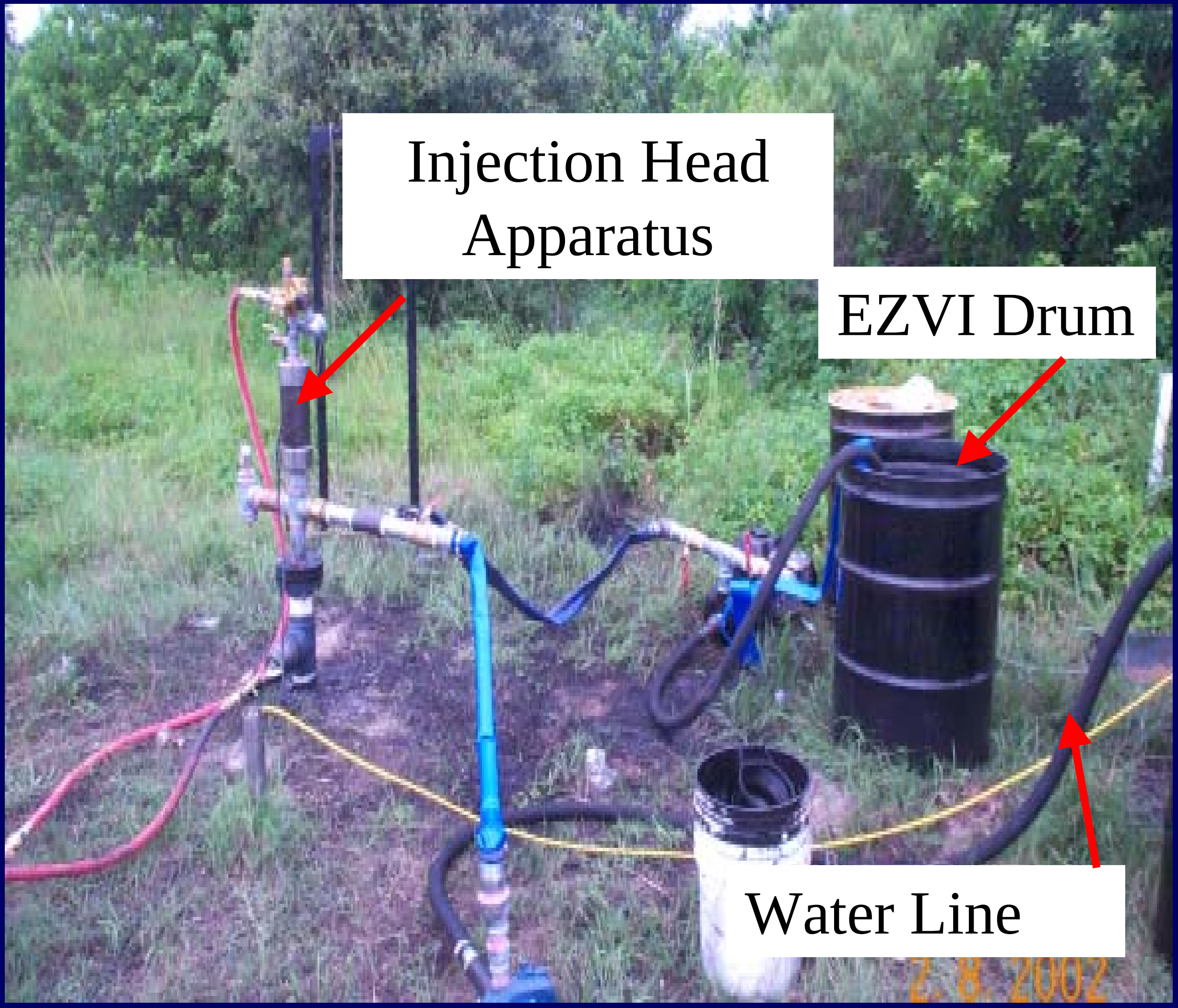
EZVI Technology Evaluation

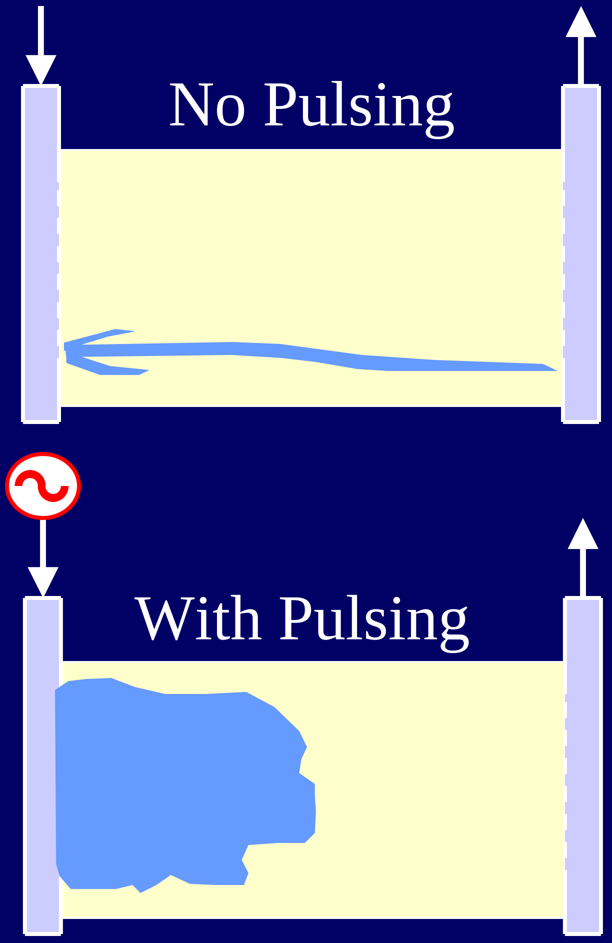
Demonstration at LC34

- A number of injection methods were tested including direct injection, pneumatic injection and pressure pulse technology (PPT).

- 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.

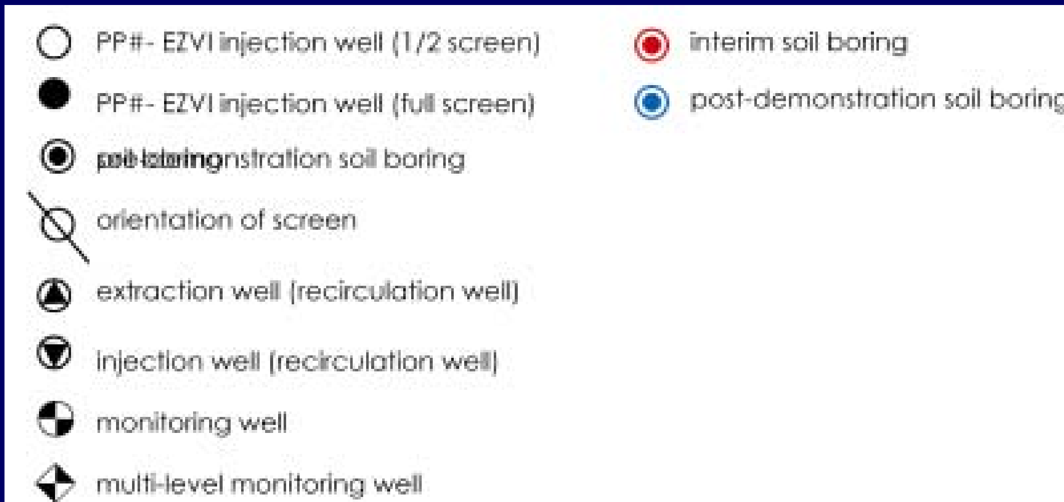
Pressure Pulse Technology





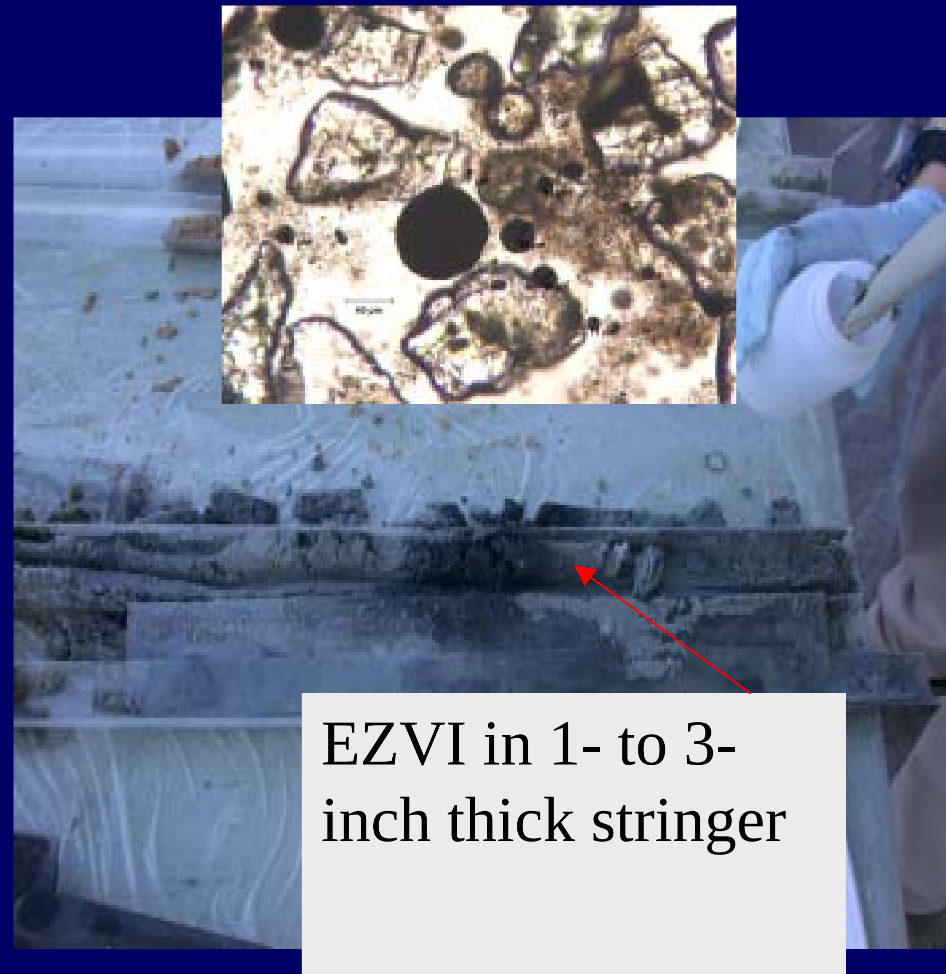
EZVI Injection Set-Up Within PTA

Interim 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

Top Depth (ft)	Bottom Depth (ft)	Pre-Demo SB-1	Post-Demo SB-301	Pre-Demo SB-3	SB-203	Post-Demo SB-303	Pre-Demo SB-4	SB-204	Post-Demo SB-304
6	8	ND	0	ND	1	0	ND	ND	0
8	10	1	1	0	NA	0	0	NA	0
10	12	1	1	0	1	1	0	0	0
12	14	3	4	1	1	1	6	1	0
14	16	6	1	7	13	4	6	1	ND
16	18	87	1	6,067	1	1	45	1	ND
18	20	282	12	209	1,023	451	161	6	2
20	22	208	8	195	798	7	171	3	1
22	24	230	0	253	495	4,502	249	35	0
24	26	283	NA	272	2	17	289	183	0
26	28	263	119	252	1	45	255	27	28
28	30	256	9	340	271	293	236	133	193

Top Depth	Bottom Depth	Pre-Demo SB-2	Post-Demo SB-302	Pre-Demo SB-7	SB-207	Post-Demo SB-307	Pre-Demo SB-8	SB-208	Post-Demo SB-308
6	8	ND	0	ND	1	0	ND	ND	ND
8	10	ND	NA	0	NA	NA	3	ND	0
10	12	ND	1	0	1	2	2	ND	1
12	14	1	1	2	ND	1	2	ND	0
14	16	10	11	70	ND	0	21	ND	NA
16	18	89	5	1,167	0	NA	127	ND	0
18	20	182	57	207	54	23	136	ND	NA
20	22	233	NA	175	ND	NA	157	NA	177
22	24	262	18	202	268	19	162	143	130
24	26	259	7	222	177	149	212	NA	125
26	28	270	8	268	252	175	237	269	NA
28	30	196	144	249	248	NA	226	NA	248
30	32	5	28	1	NA	235	47	NA	NA

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

Results of Demo at LC34

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

On-Going/Up-coming Work

So….Ongoing research includes:

- Injection testing to improve ability to deliver EZVI to source zone

- More research on determining % of degradation due to ZVI and biodegradation

Upcoming Work

Evaluation and Selection of Injection Methods

- NASA Funded Evaluation of Injection Methods:
  - Fall of 2003 at LC34
  - Four injection methods
- Injection Technologies to be Evaluated:
  - Hydraulic fracturing
  - Pneumatic fracturing
  - Pressure Pulse Technology
  - Direct injection

Upcoming Work

Evaluation and Selection of Injection Methods

Hydraulically placed sand filled fracture

Hydraulic Fracturing

Upcoming Work

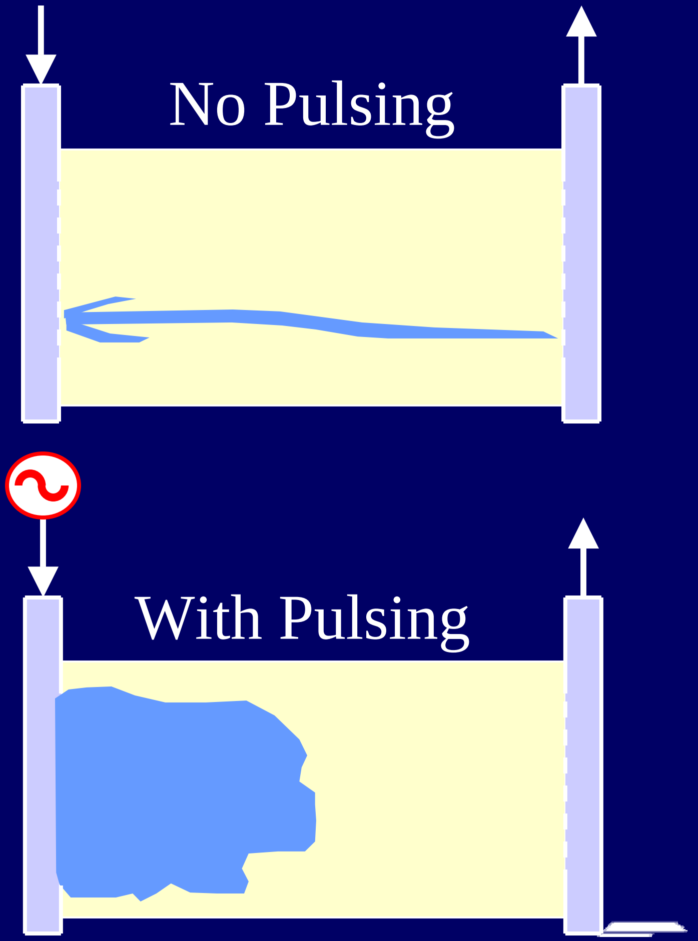
Evaluation and Selection of Injection Methods

Pneumatic Fracturing

EZVI being pumped from injection nozzle

EZVI being atomized from injection nozzle

Pressure Pulse Technology



Upcoming Work

Evaluation and Selection of Injection Methods

Direct Injection