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

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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.**

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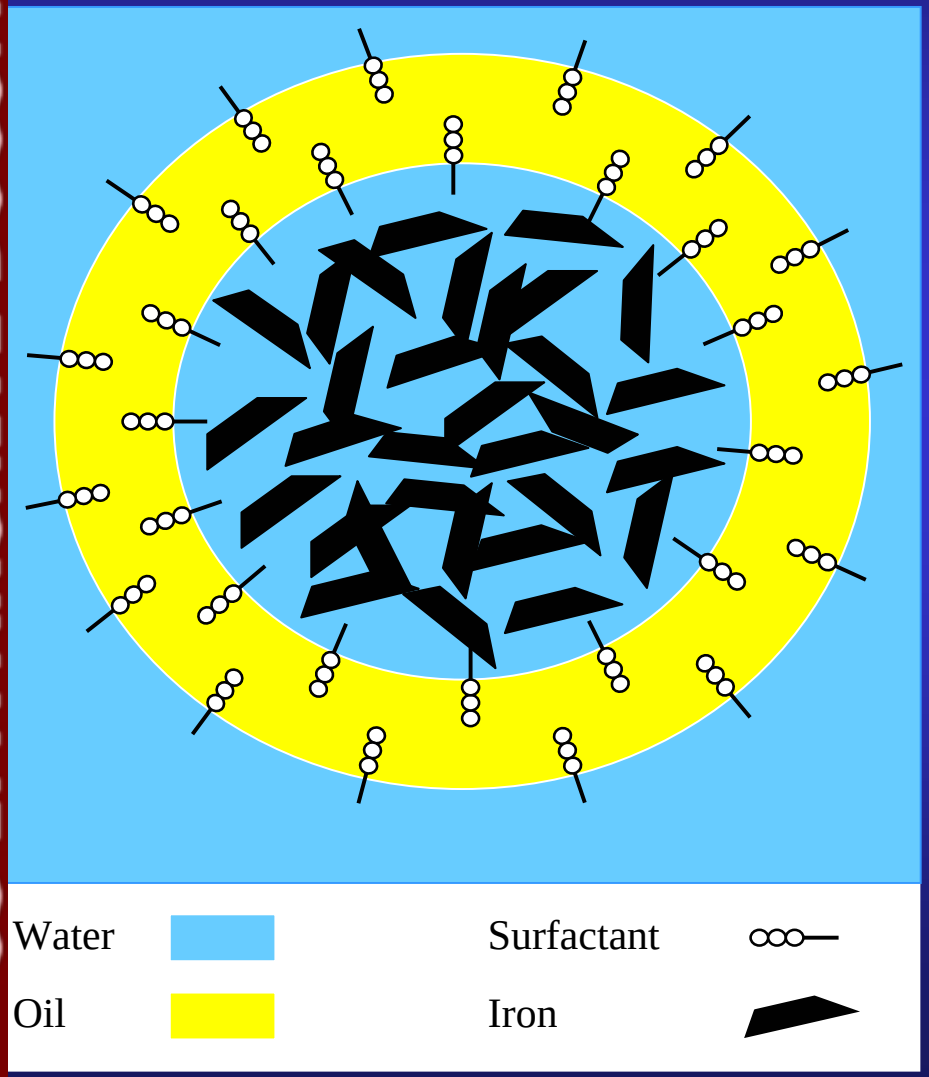
Properties of EZVI



- 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)

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Properties of EZVI

- EZVI's exterior oil membrane has hydrophobic properties similar to DNAPL, and is therefore 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; promoting anaerobic biodegradation.

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Properties of EZVI
In Contact with DNAPL

DNAPL
dyed red

DNAPL with micro-
scale ZVI

DNAPL with
EZVI

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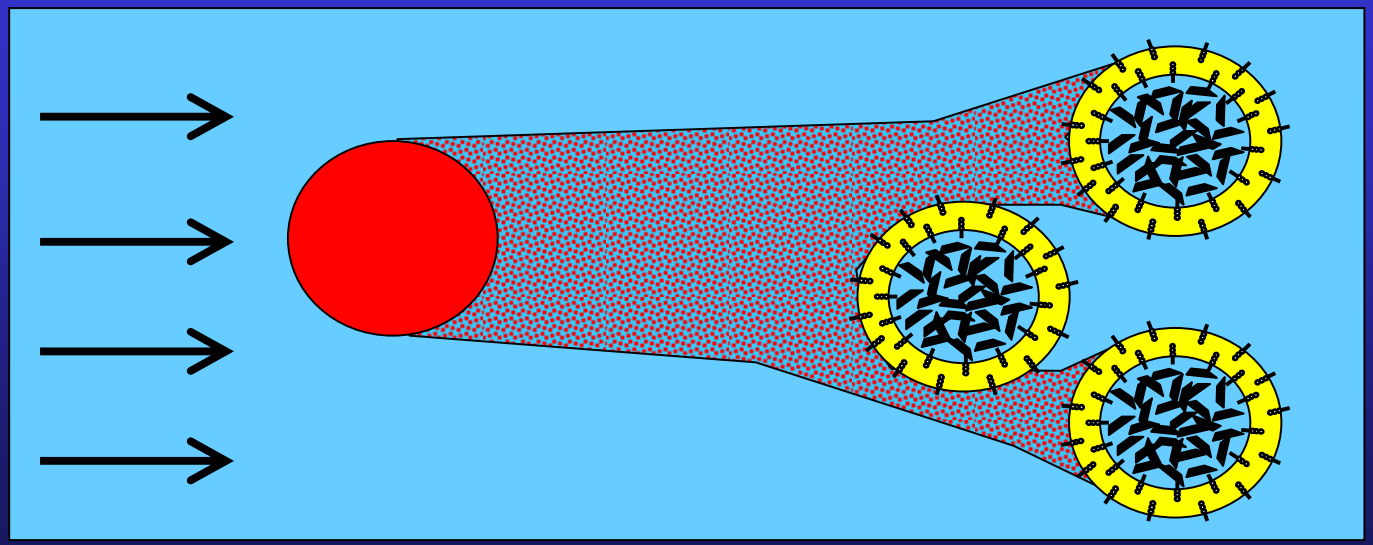
Properties of EZVI
In Contact with Dissolved Phase

- 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.



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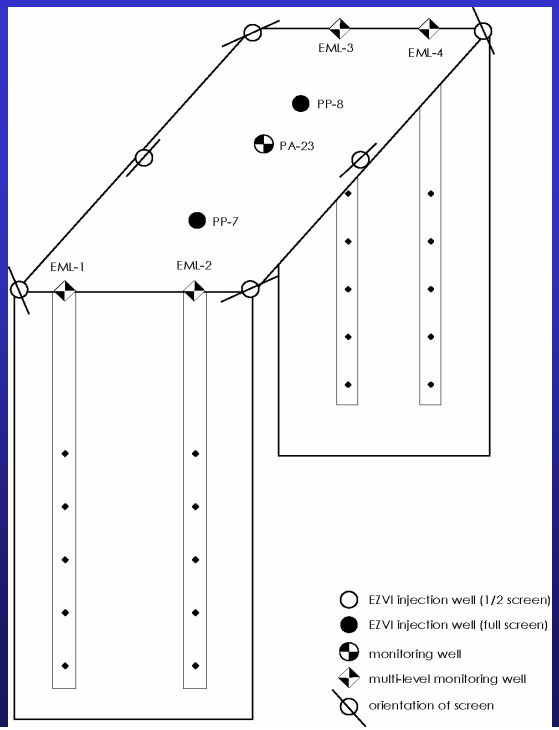
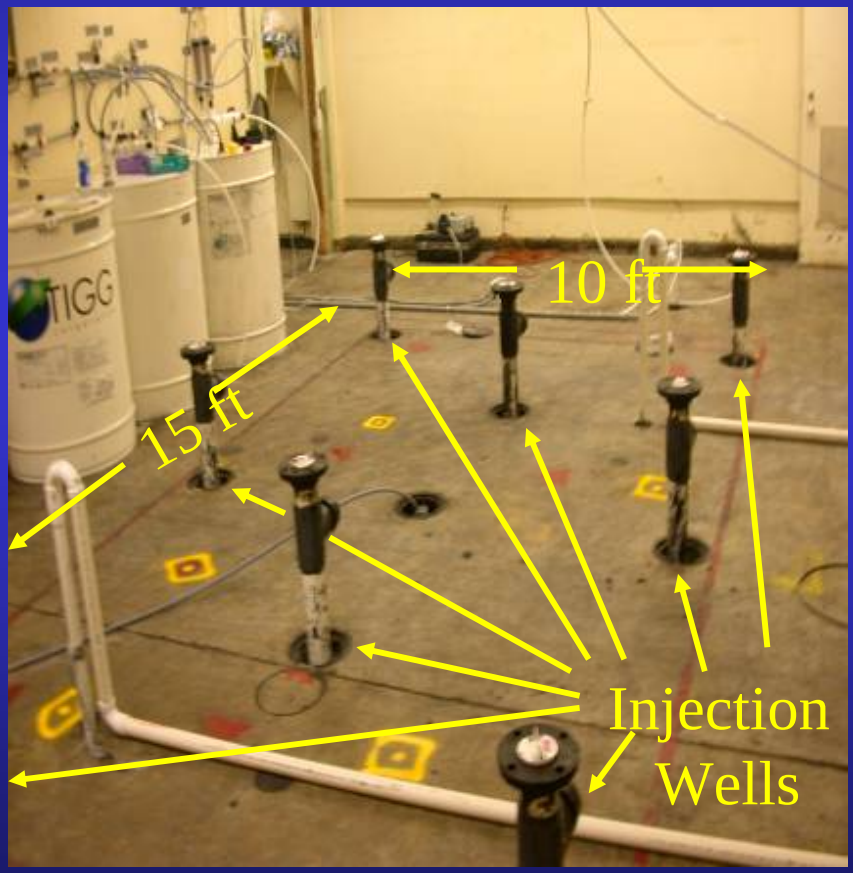
EZVI Injection Set-Up Within PTA

- **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**





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EZVI Injection Set-Up Within PTA

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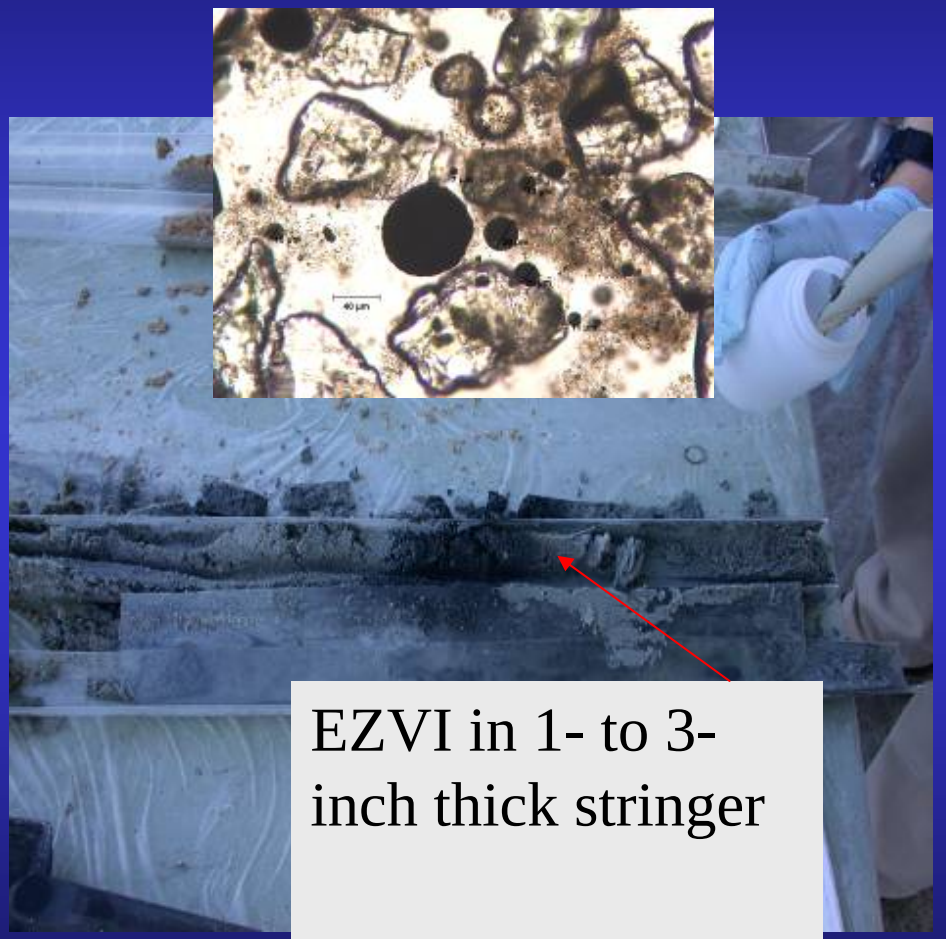
Results of Demo at LC34

Soil Core Samples:

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



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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
- **Overall results met the stated objective <u>but</u> were lower than believed possible due to injection control issues.**
  - Performed follow-on injection testing and found direct injection and pneumatic injection had best performance for use with EZVI.
- **Elevated cis-1,2-DCE, VC suggest biodegradation due to oil as an electron donor may also be a significant bonus.**

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Further Lab Testing of EZVI

- Lab tests conducted to evaluate treatment of dissolved and DNAPL-phase TCE (10 x saturation) using:
  - Active Control
  - Vegetable oil & surfactant (Emulsion)
  - Nano-scale zero-valent iron (nZVI)
  - Emulsified zero-valent iron (EZVI)
- Monitor VOCs, DHG and Chloride
- Work funded by ESTCP

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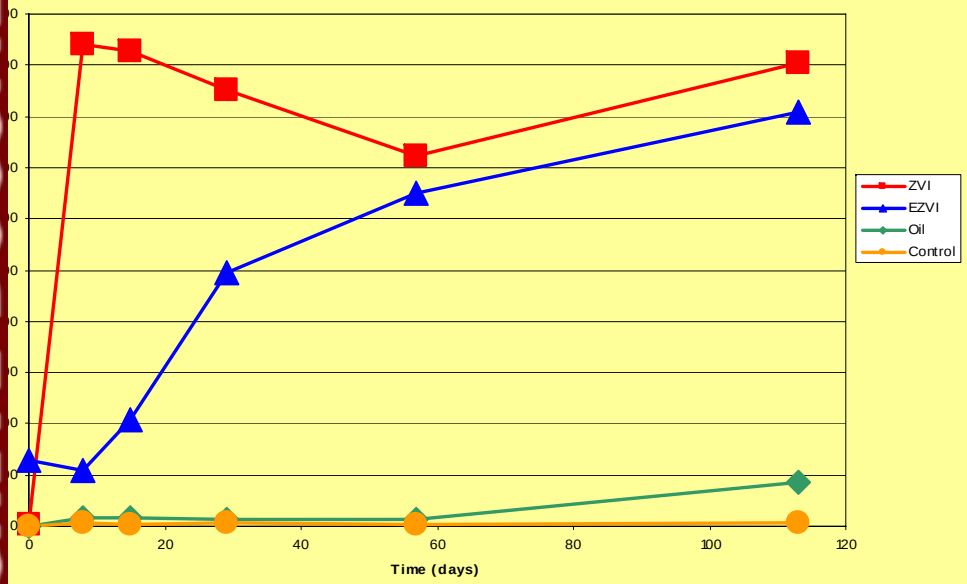
Chloride Production

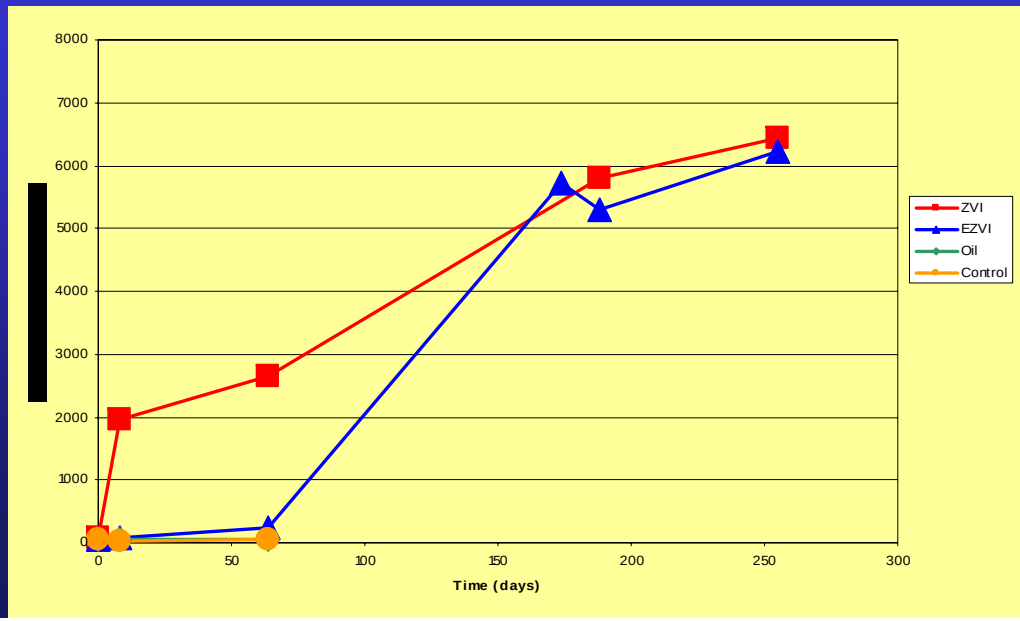


Dissolved-Phase

- TCE completely degraded using both nZVI and EZVI.
- Both achieved similar results in the same time period.

DNAPL-Phase

(data to date)



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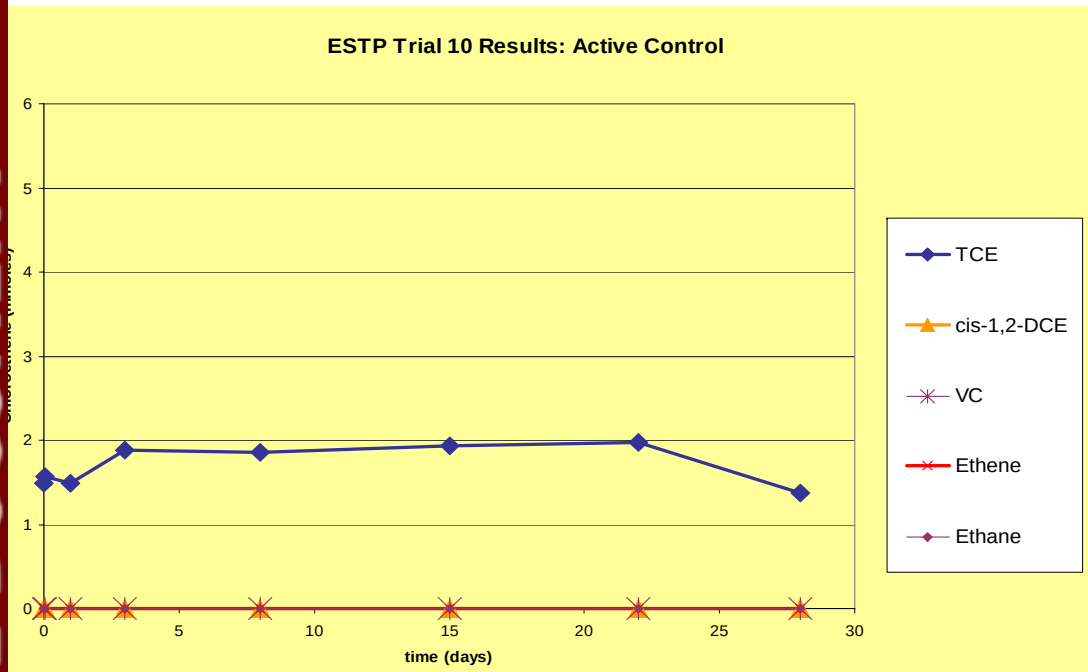
DNAPL

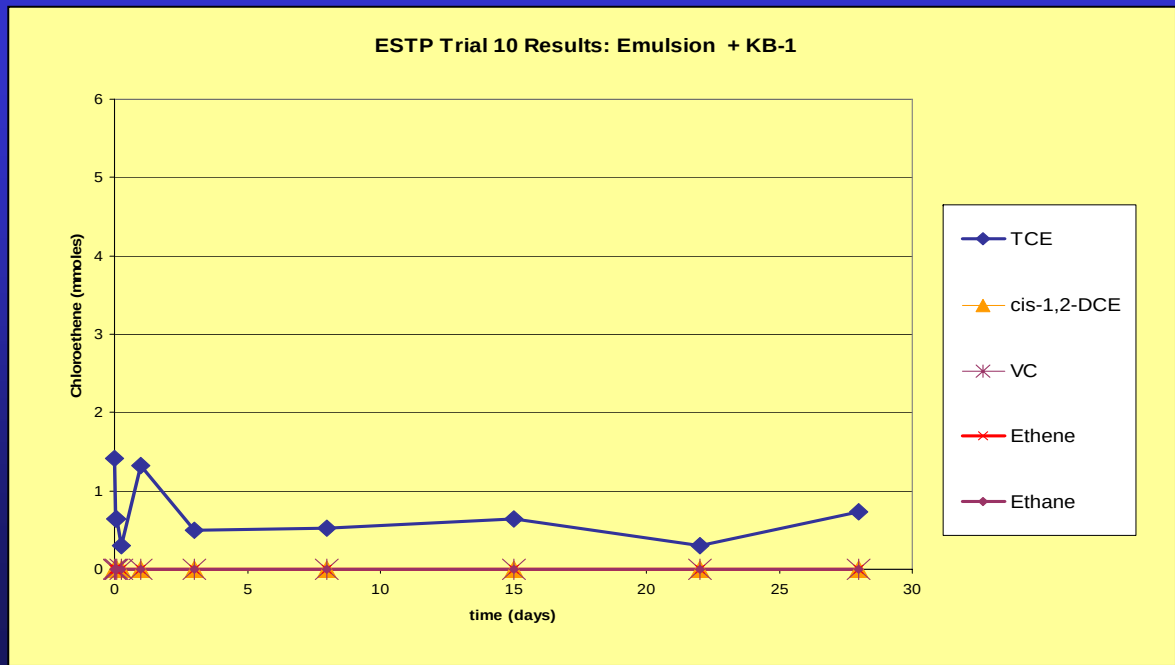


Active Control

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

Veg 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



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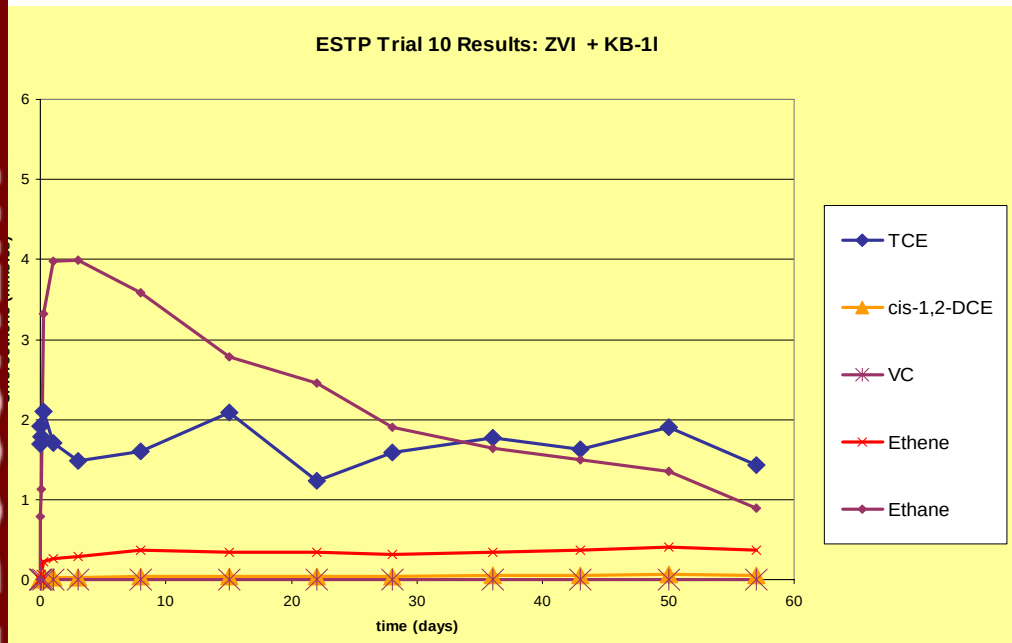
DNAPL

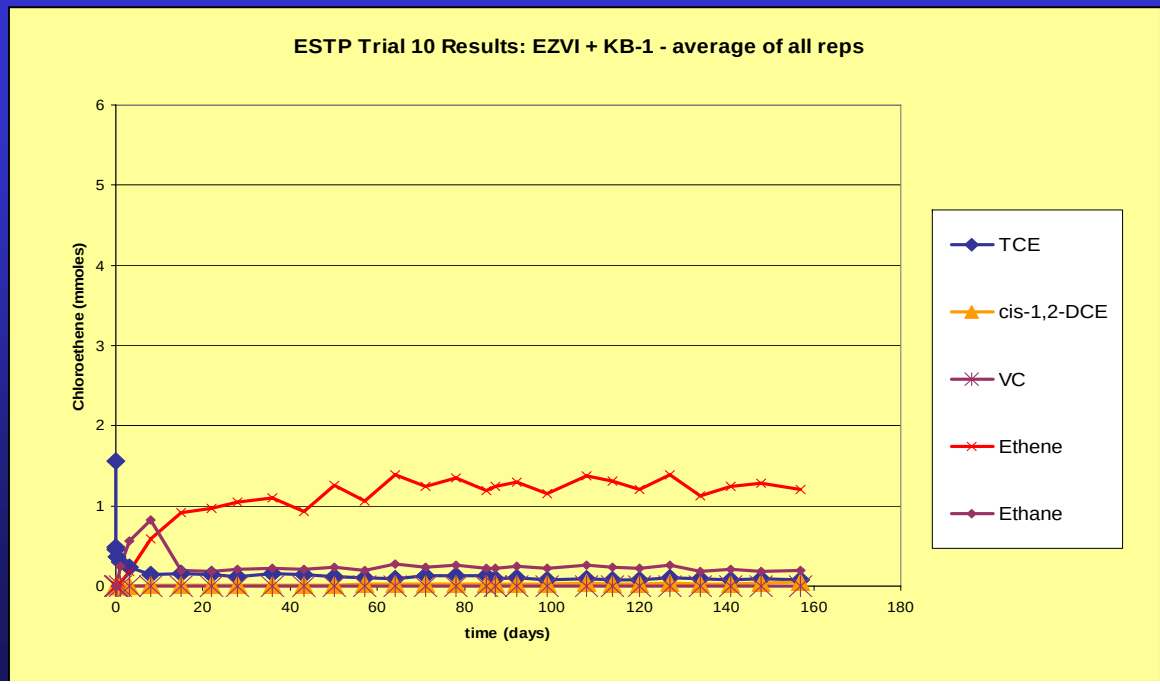


nZVI Treatment

- TCE stable at saturation concentration
- Degradation by-products observed (ethane and ethene)
- Chloride production indicates degradation of ~65% of TCE

EZVI Treatment

- TCE ~10% of saturation concentration and dropping
- Degradation by-products observed (ethane and ethene)
- Chloride production indicates degradation of ~62% of TCE



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Conclusions of Lab Test

- Veg Oil Emulsion drops TCE concentration due to sequestration (no degradation).
- nZVI reduces mass of TCE due to treatment but no drop in concentration of TCE.
- EZVI benefits from sequestration due to oil plus degradation due to nZVI (drop in concentration and reduction in mass).
- Impacts of biodegradation not significant in these tests which utilized DI water and no soil (expect to see biodegradation with emulsion and EZVI).