

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

**Jacqueline Quinn, NASA**

**Suzanne O'Hara, Thomas Krug, GeoSyntec Consultants;**

**Christian Clausen, Cherie Geiger, University of Central Florida;**

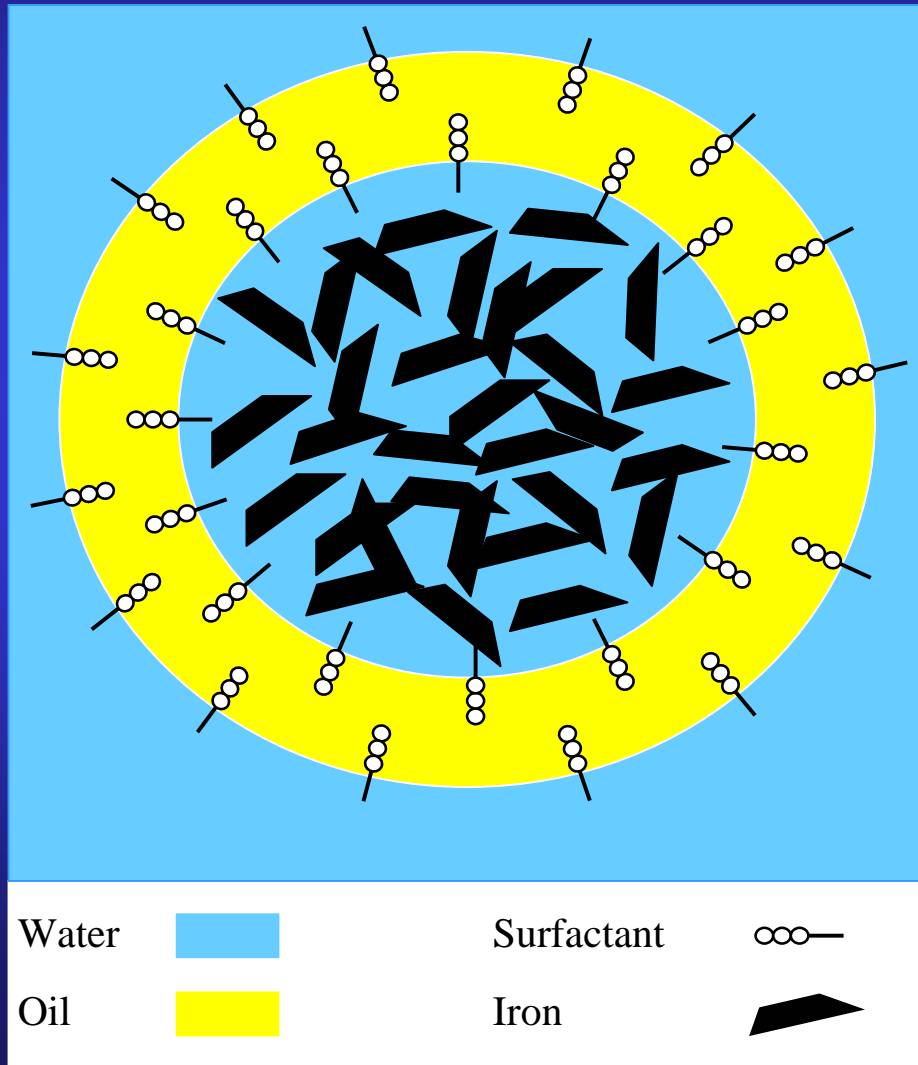
**Kathleen Brooks, ASRC**

# 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.**



# 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



- 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.

# Properties of EZVI In Contact with DNAPL



DNAPL  
dyed red



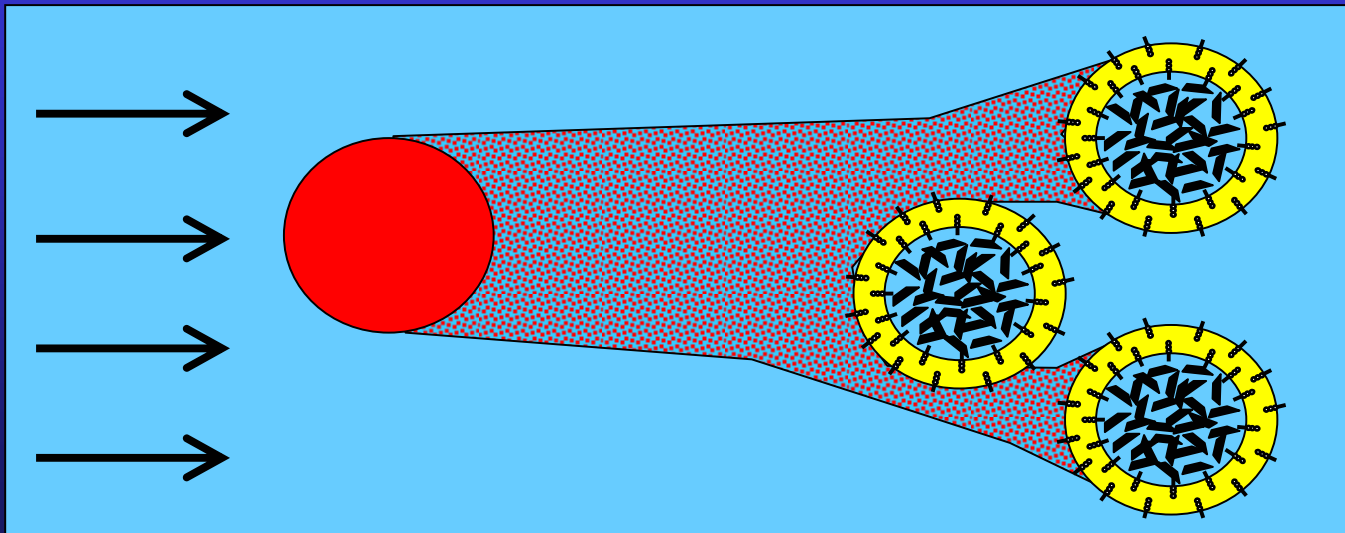
DNAPL with micro-  
scale ZVI



DNAPL with  
EZVI

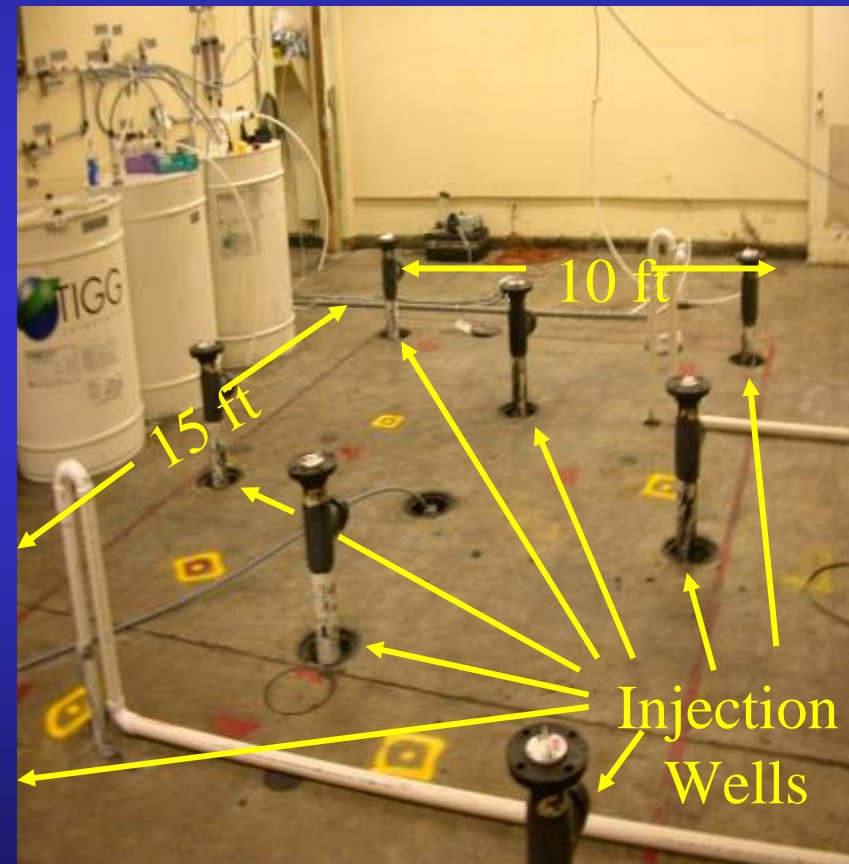
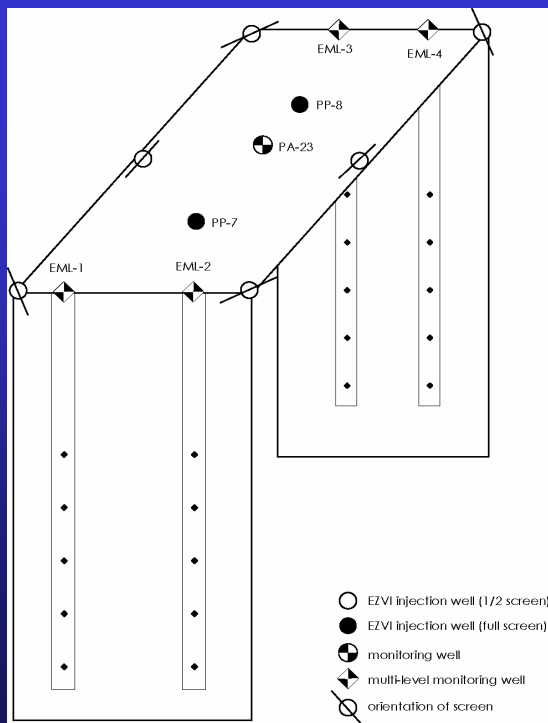
# Properties of EZVI In Contact with Dissolved Phase

- 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 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



# EZVI Injection Set-Up Within PTA



No Pulsing

With Pulsing

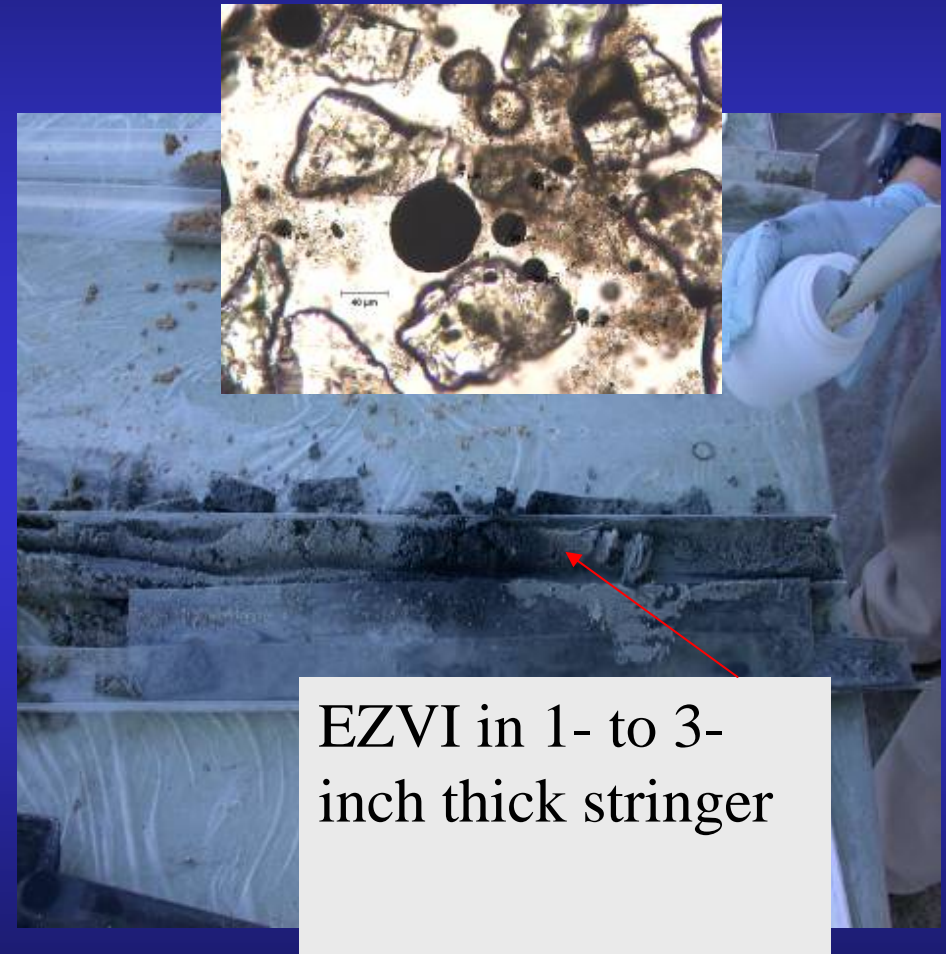
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# Results of Demo at LC34

## ➤ 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



# 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<sup>2</sup>/day down to 8.5 mmoles/ft<sup>2</sup>/day

## ➤ Overall results met the stated objective but were lower than believed possible due to injection control issues.

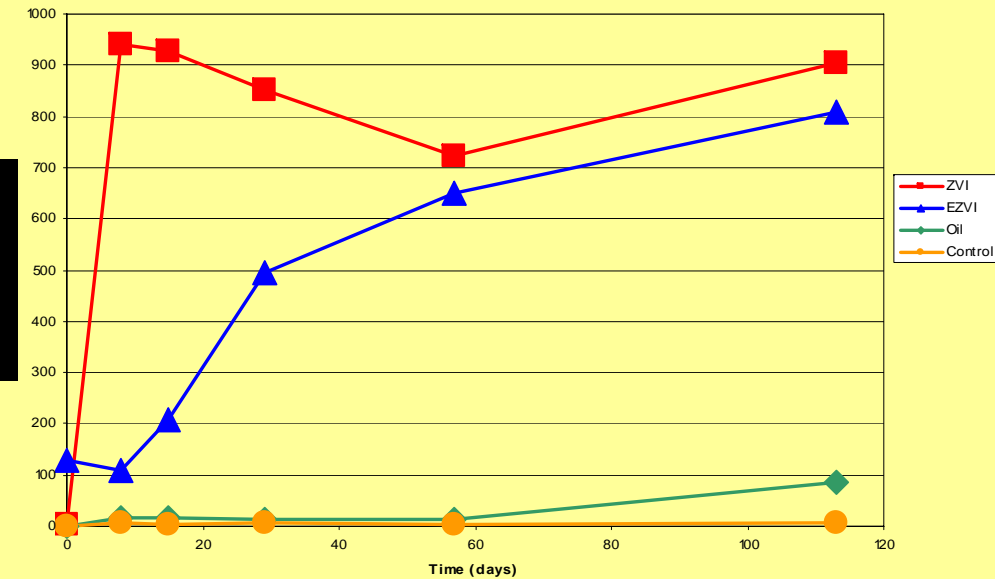
- Performed follow-on injection testing and found direct injection and pneumatic injection had best performance for use with EZVI.

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

# 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

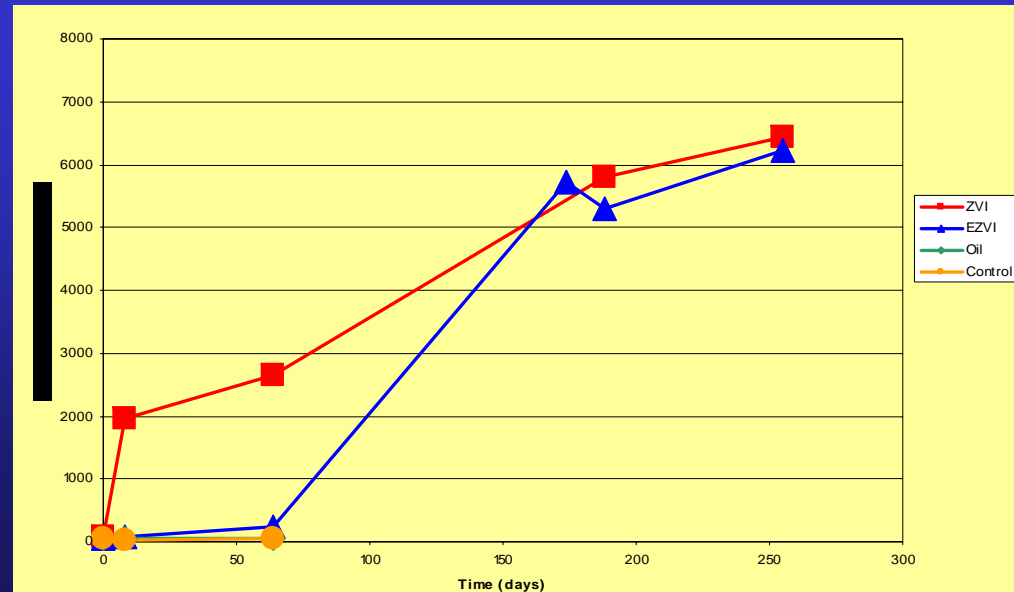
# Chloride Production



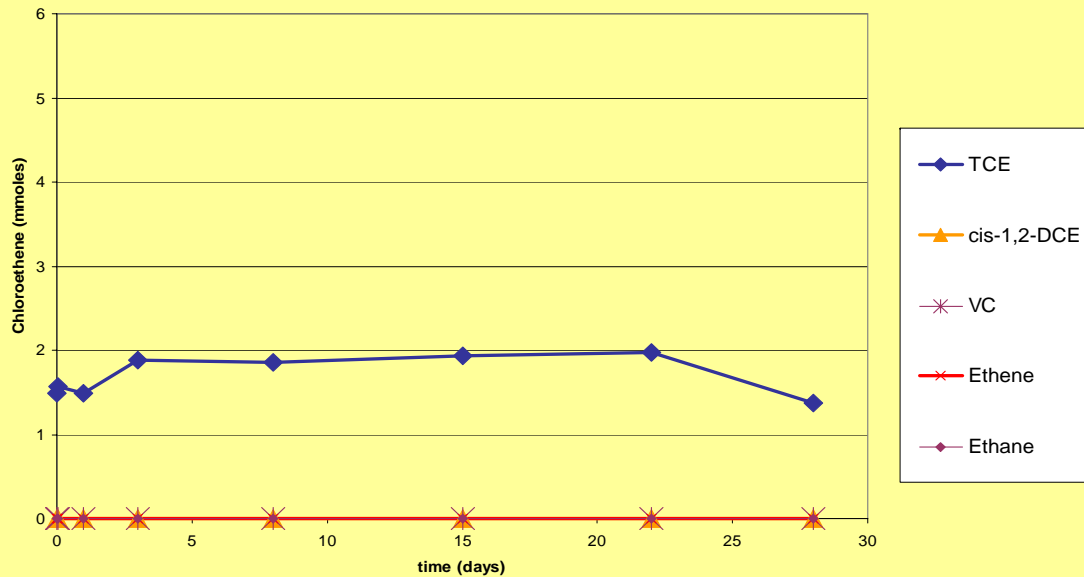
## DNAPL-Phase (data to date)

### Dissolved-Phase

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



ESTP Trial 10 Results: Active Control



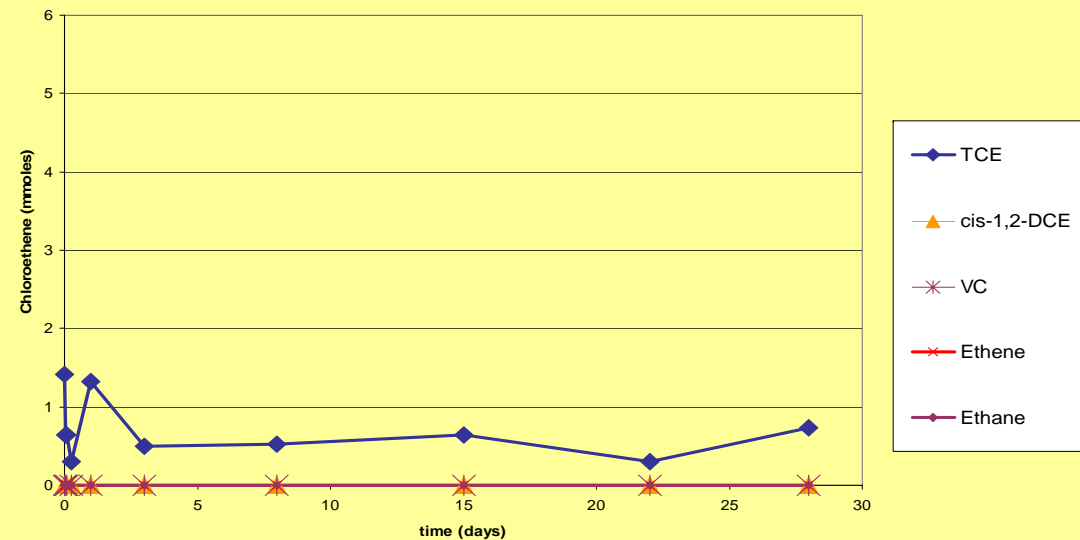
## Active Control

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

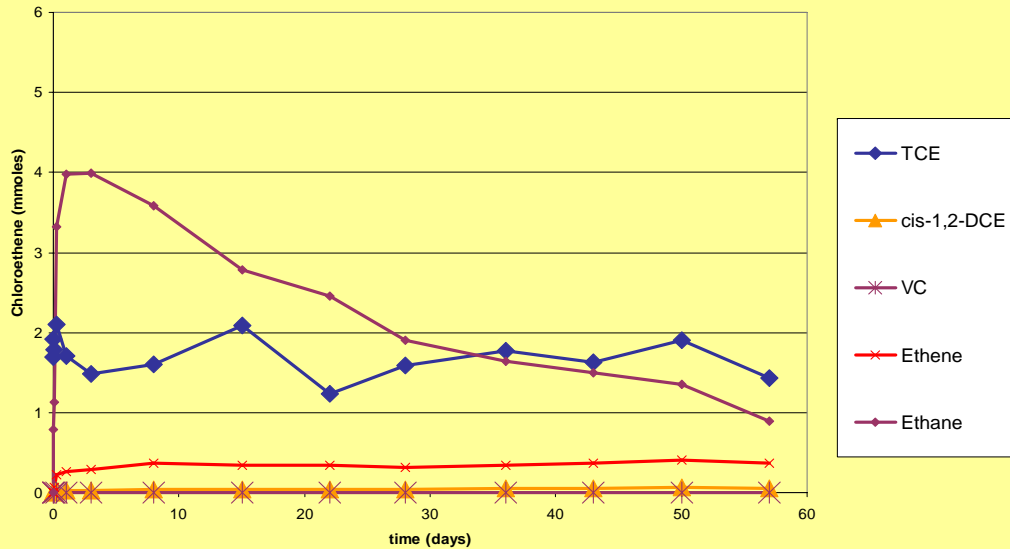
## Veg Oil Emulsion Treatment

- 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

ESTP Trial 10 Results: Emulsion + KB-1



ESTP Trial 10 Results: ZVI + KB-1I



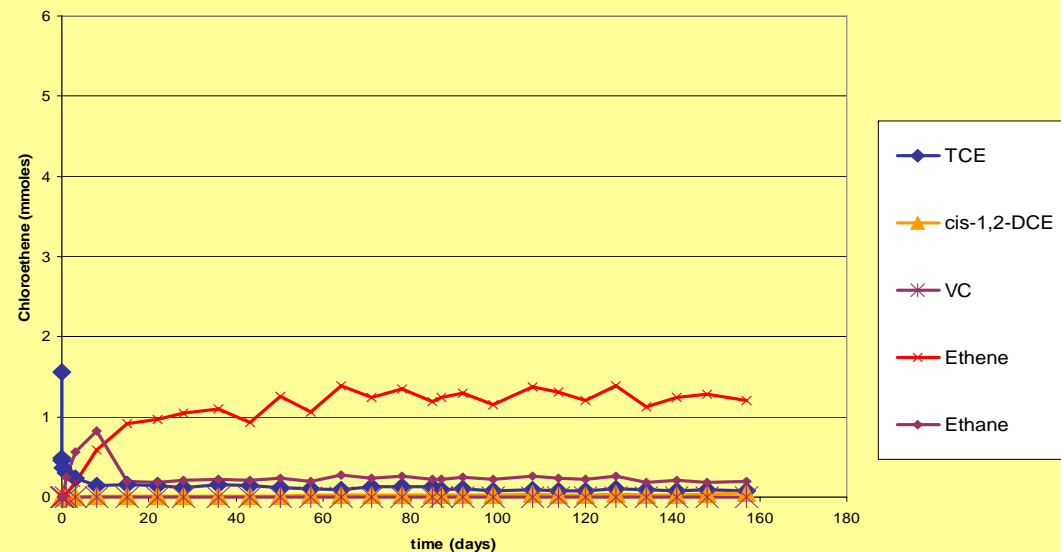
## nZVI Treatment

- 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

ESTP Trial 10 Results: EZVI + KB-1 - average of all reps



# 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).