In Situ DNAPL Destruction with the EZVI Technology: Lessons Learned and Recent Advancements

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Presentation Outline

- Background and History
- Technology Description
- Implementation
- Case Studies – 2
- Lessons Learned
- Technology Update – Product Optimizations
- Summary

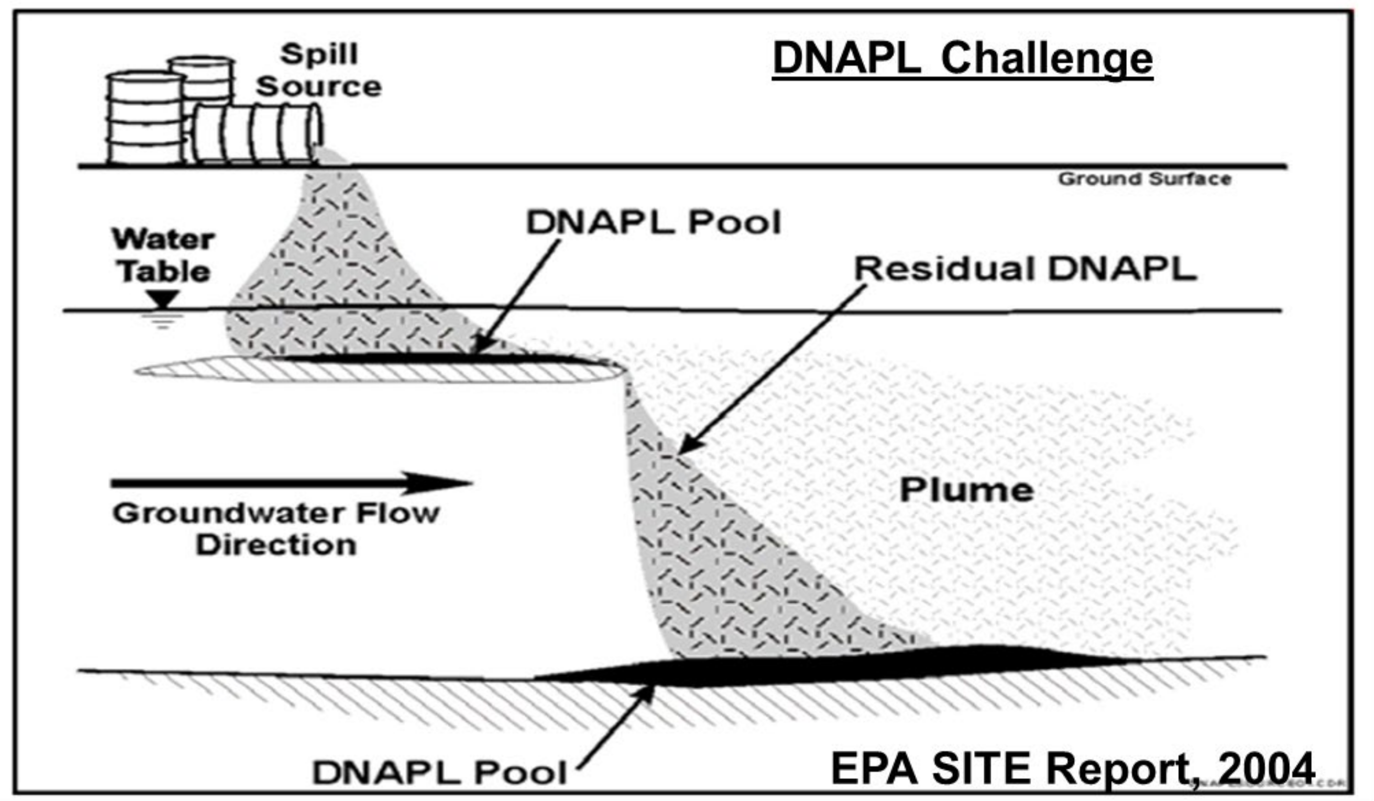
Presentation GOAL:

For you to gain a good understanding of what the EZVI technology is, when it is an appropriate remedial alternative and what are the most recent advancements to the technology.

Background – The Nature of the Problem

History – DNAPL Remediation Issues

- **Physical Chemistry**
  - Hydrophobic
  - Density & Viscosity
  - Low Water Solubility
- **Location**
  - Precision
- **Treatment**
  - Contact



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Background – Development Timeline

DEVELOPMENTS TO DATE

1997 – 1998: Conceptualization/Development

1999 – 2001: Proof of Concept R&D at UCF/KSC

2002 – 2004: Pilot studies – EPA SITE Evaluation

2005 – 1st FULL SCALE implementation – PAFB

2005 – Present: Various Applications across USA, Canada, EU

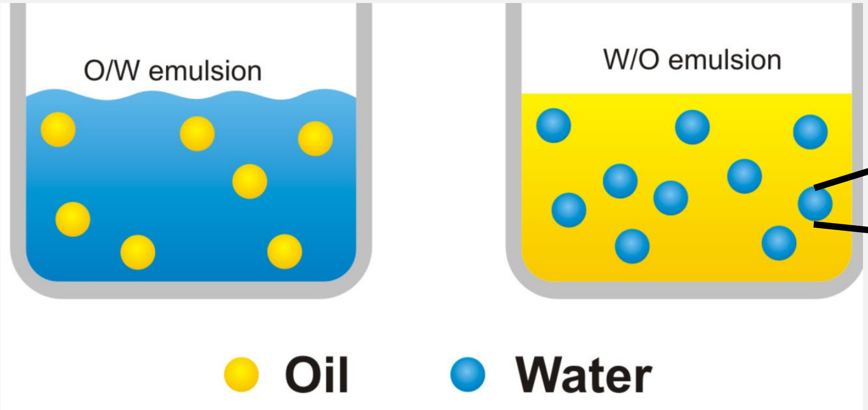
2016 – Technology Enhancement **- Biotic Processes** – methane control

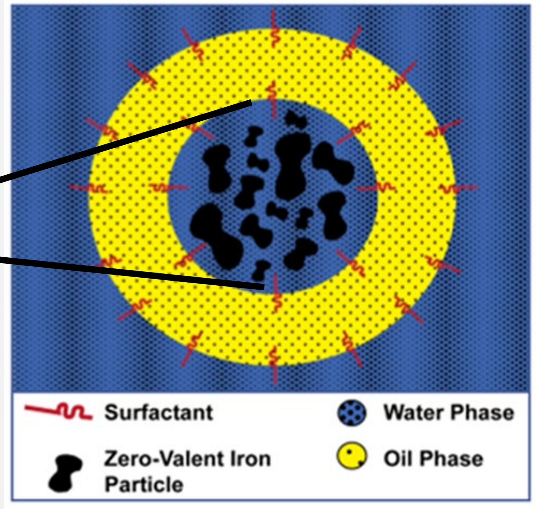
2019 – Technology Enhancement **- Abiotic Processes** – catalyzed ZVI

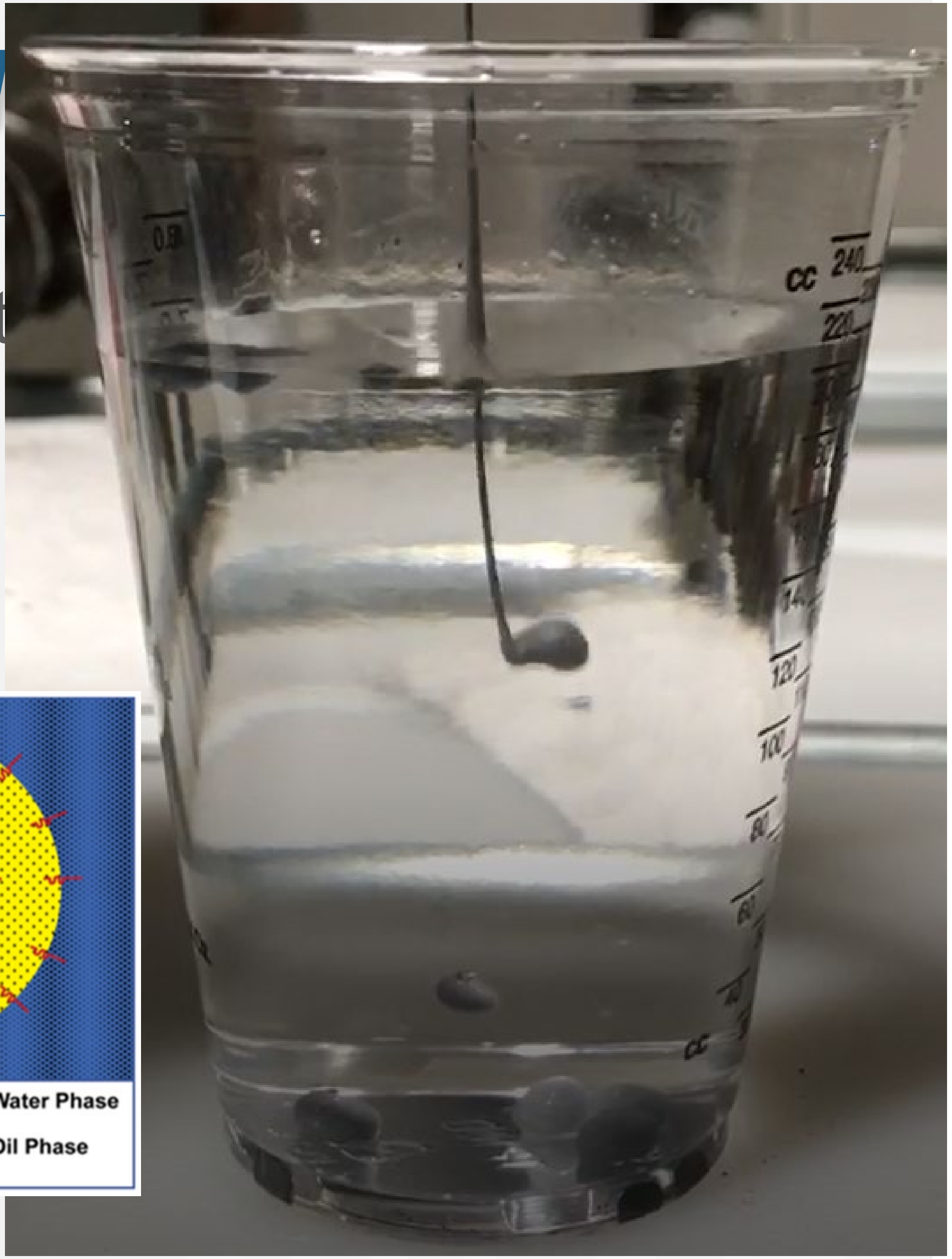
Technology Description – W

- Surfactant stabilized, <u>water-in-oil</u> emulsificat
  ZVI particles suspended in the water drops

- EZVI is a DNAPL (hydrophobic, sinker)

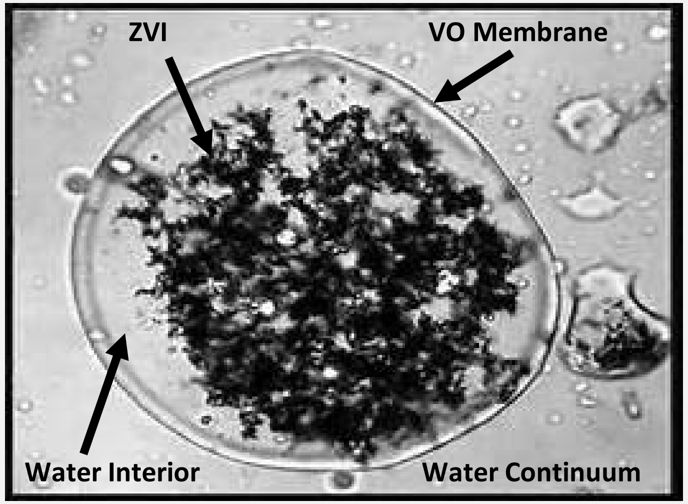


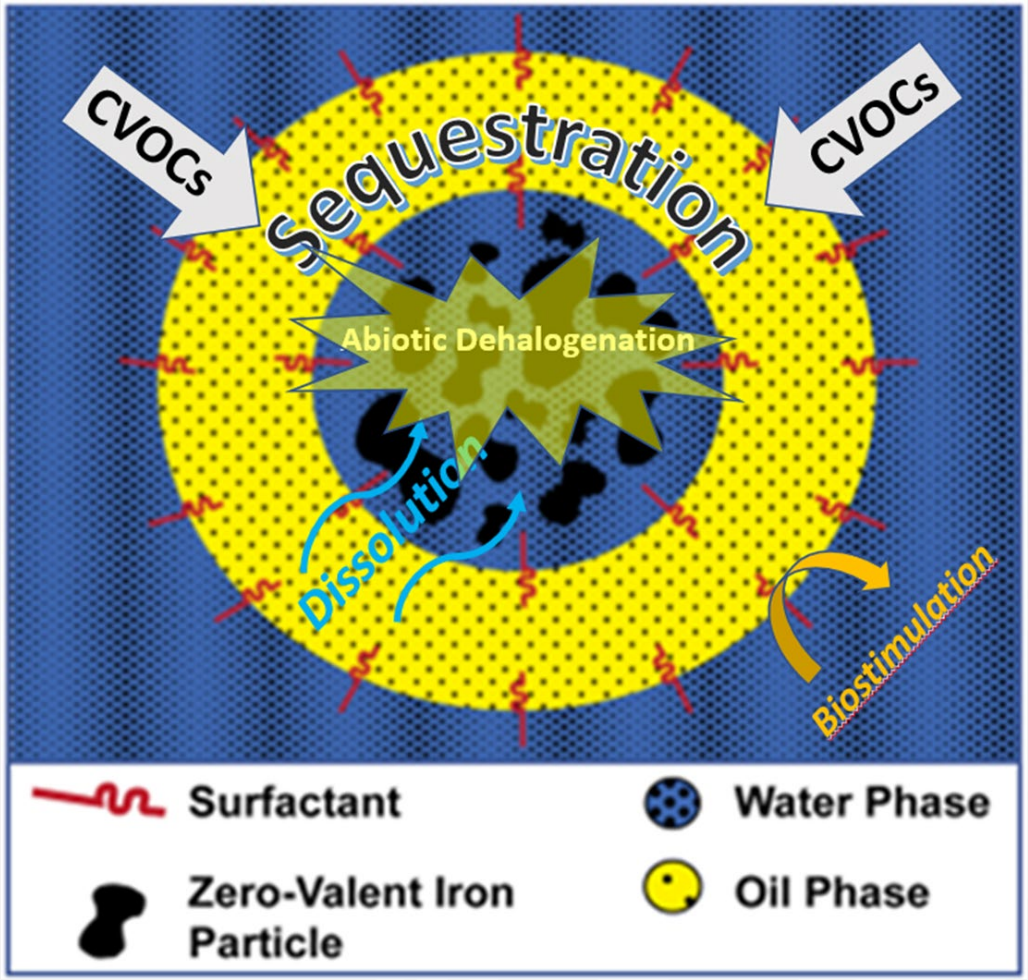




Technology Description – How Does it Work?

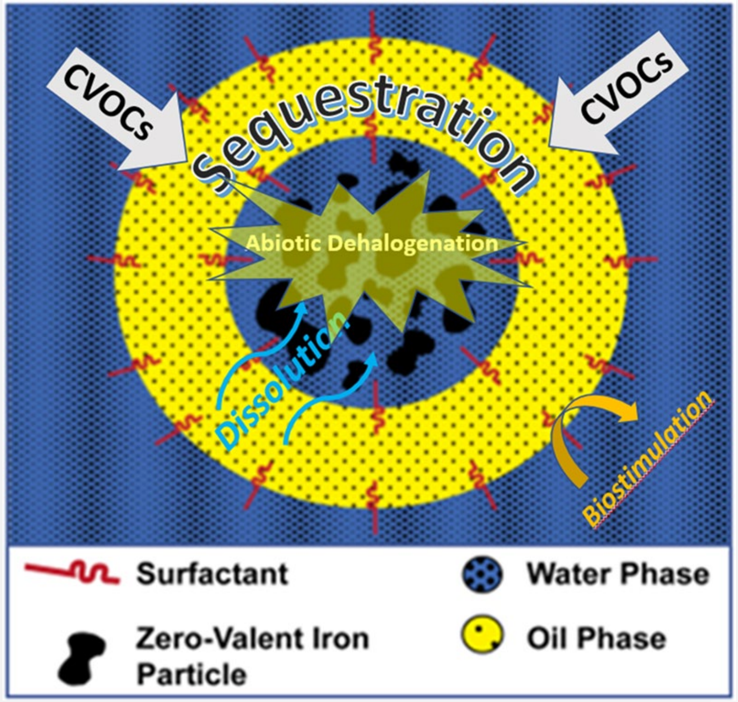
- **EZVI Processes**
  - Sequestration
  - Dissolution
  - Reductive dehalogenation (abiotic & biotic processes)
- Emulsion **Structure** is KEY

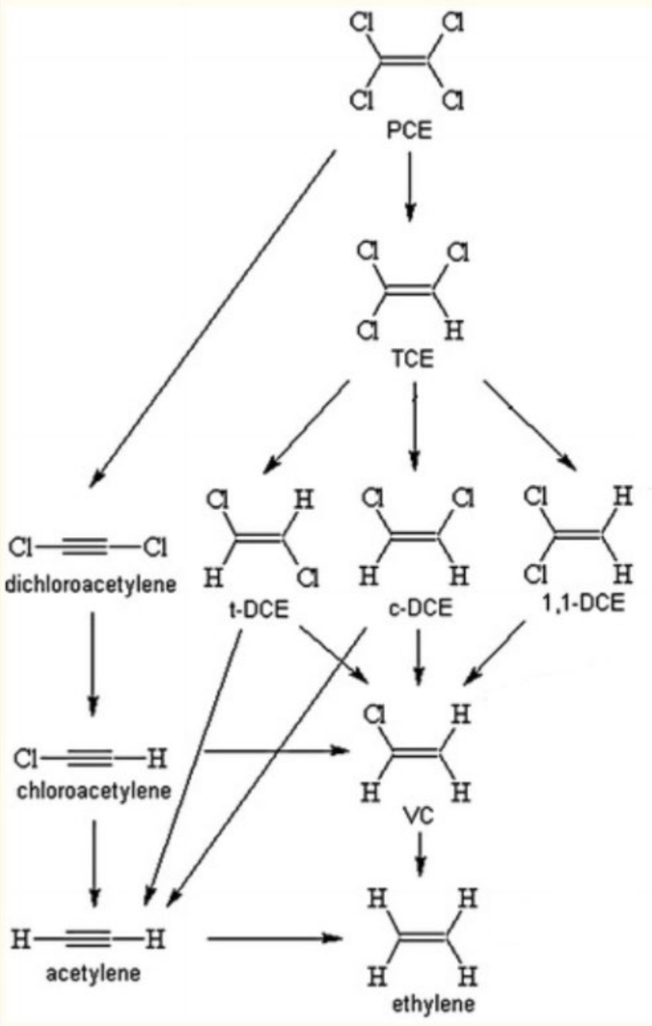




Technology Description – How Does it Work?

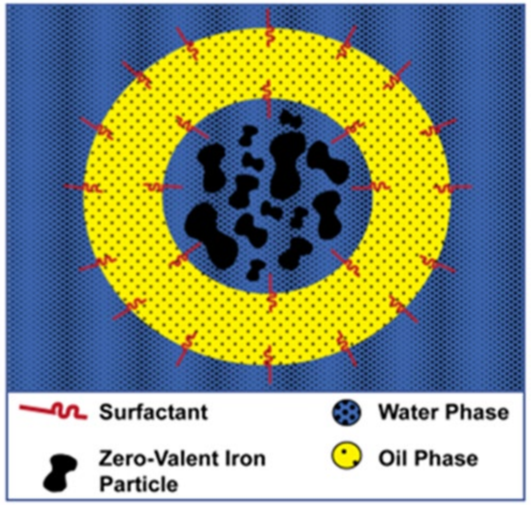
- **Reductive Dechlorination**
  - **Abiotic Processes:**
    - Interior of emulsion
    - Targeted use of ZVI
  - **Biotic Processes:**
    - Exterior of emulsion
    - Downgradient

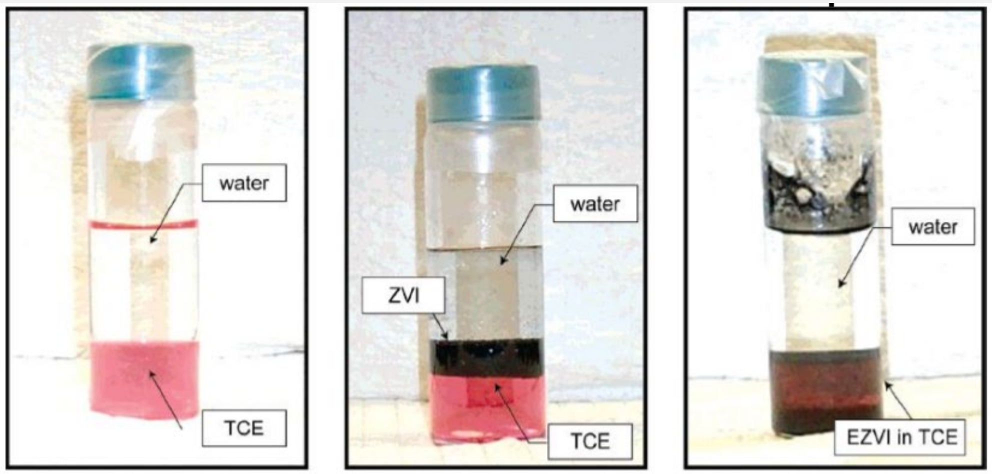




Technology Description – What is the Innovation?

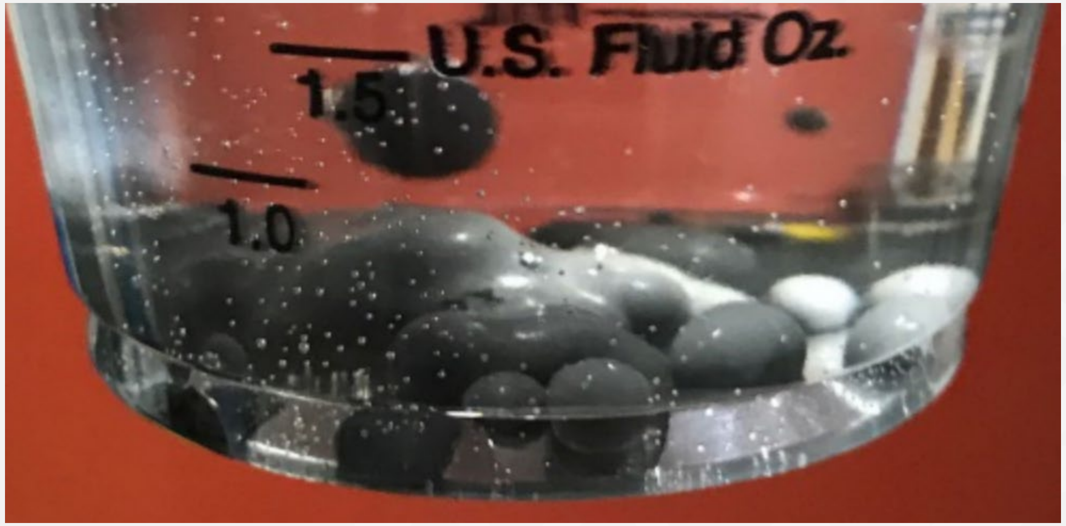
- **Miscibility** with DNAPLs
- **Combination Technology** utilizing abiotic & biotic processes AND physical chemistry
- Emulsion **structure** is key





Miscible with DNAPL

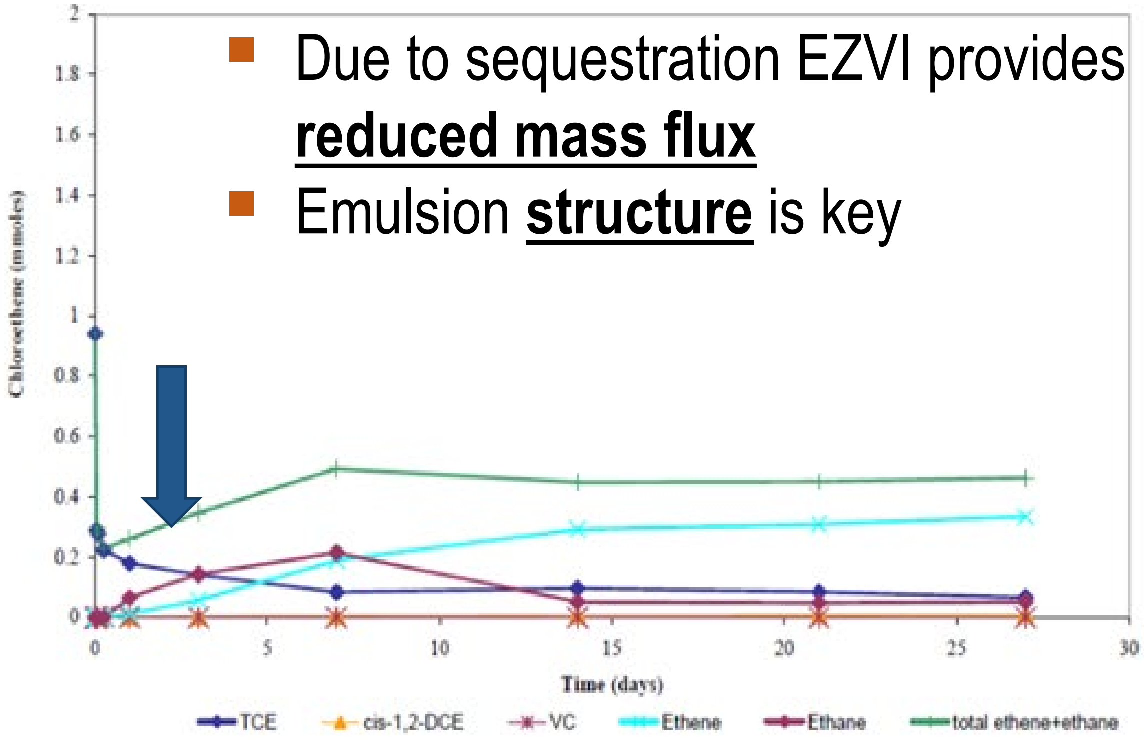
Ref: Brooks et al., 2000



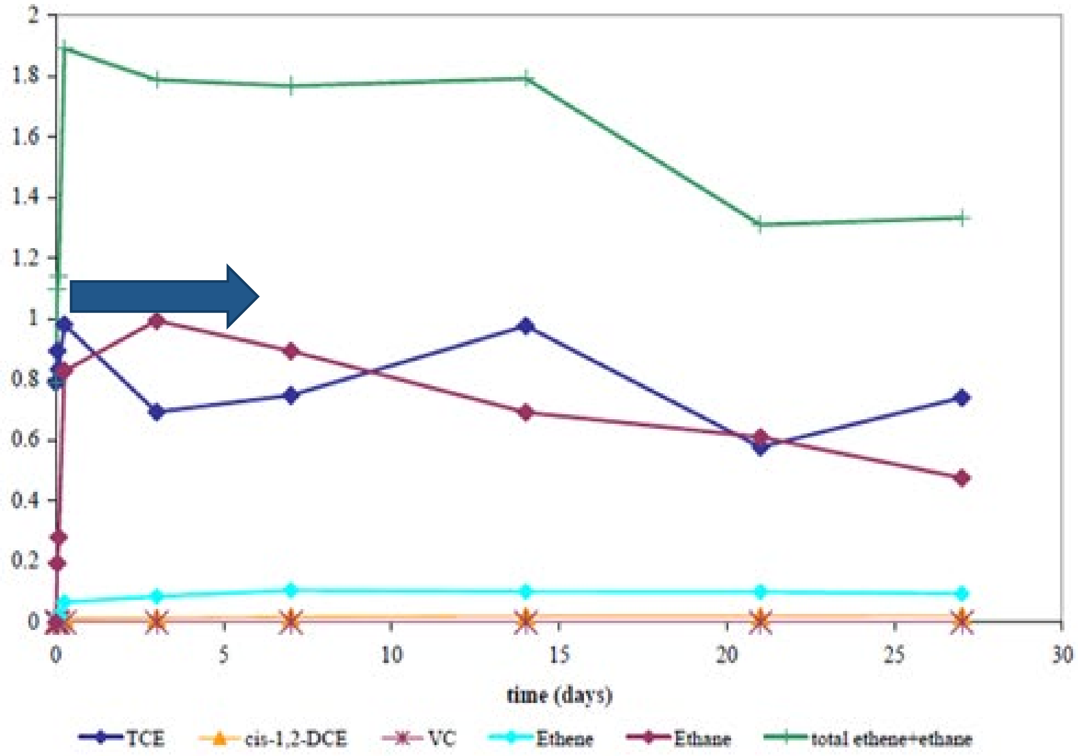
Technology Description – How is it Unique?

Utilizes Contaminant Physical Chemistry

- Due to sequestration EZVI provides **reduced mass flux**
- Emulsion **structure** is key



EZVI and KB-1 DNAPL



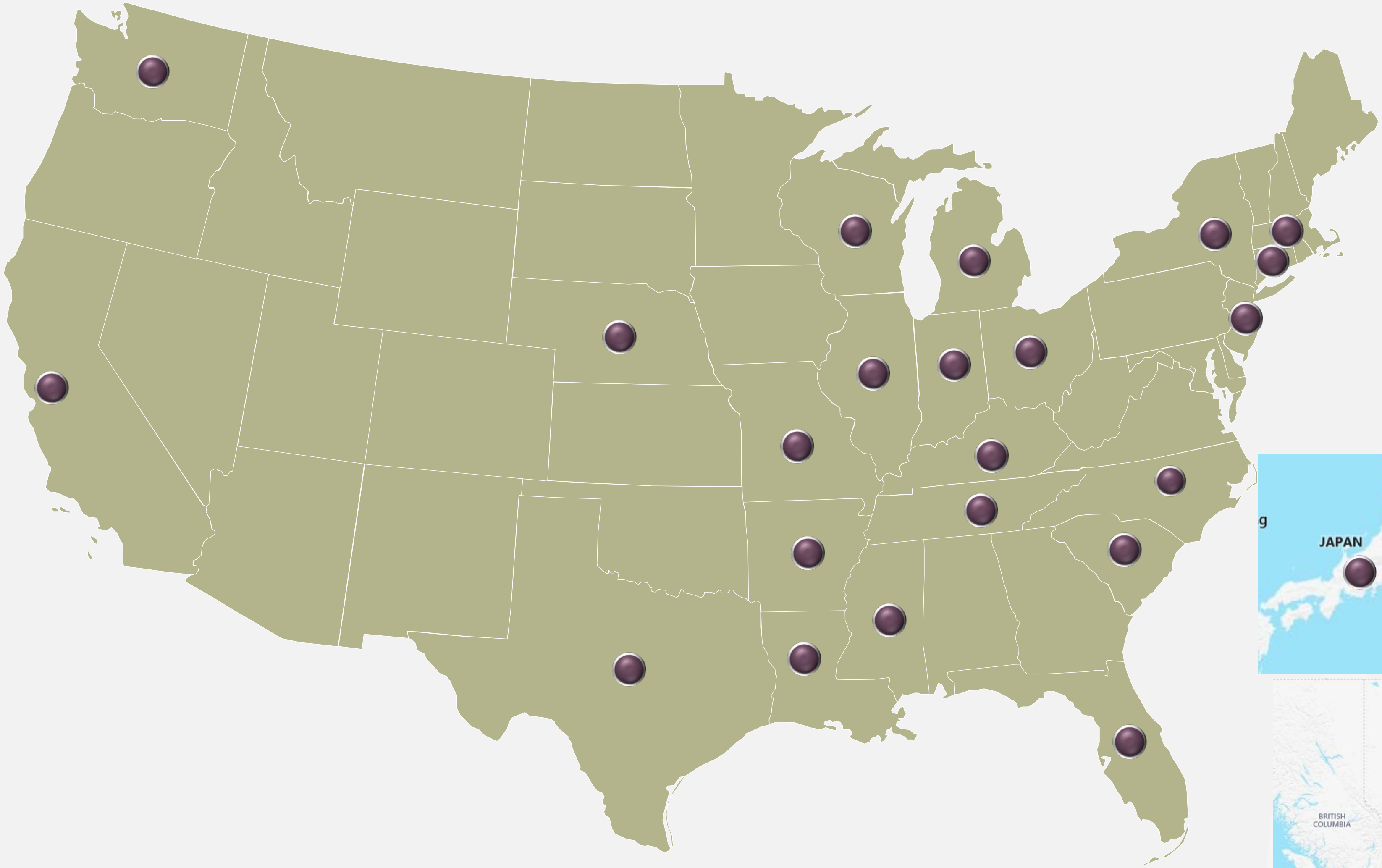
ZVI and KB-1 DNAPL

Ref: O'Hara et al., 2005

Implementation – When, Where, How?

- Engineered as an ***in situ*** **source area destruction technology**
- Implemented directly into source area soils
- Effective in **VADOSE** and **SATURATED** soils
- EZVI delivered via:
  - ➢ Pneumatic Enhanced IDS
  - ➢ Hydraulic & Pneumatic Emplacement
  - ➢ Soil Mixing

Implementations – USA & International



Implementation – FAQ's

- **When is EZVI an option?**
  - DNAPL is present
    - Parent compound(s) ≥ 10% of water solubility
  - We have access to DNAPL area
  - We have time

- **How much do I need?**
  - Dosing driven by distribution/subsurface contact vs stoichiometry
  - Target ~ 8 - 15% of effective pore space

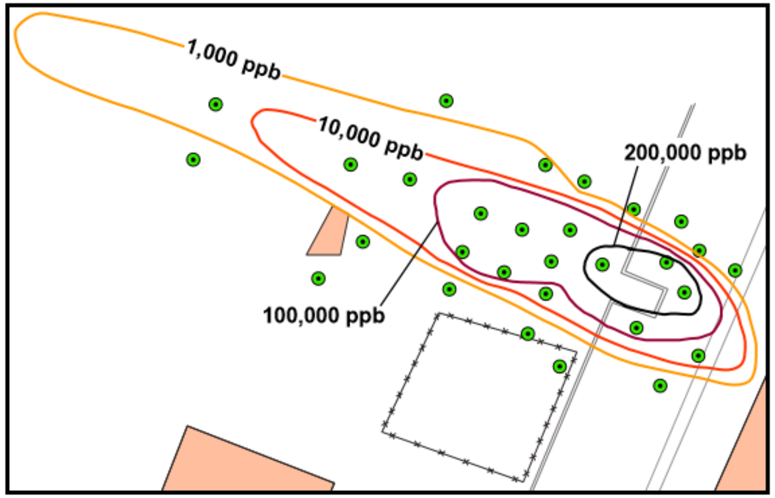
- **Can EZVI be injected through well screens?**
  - Not recommended
  - Minimizes efficacy

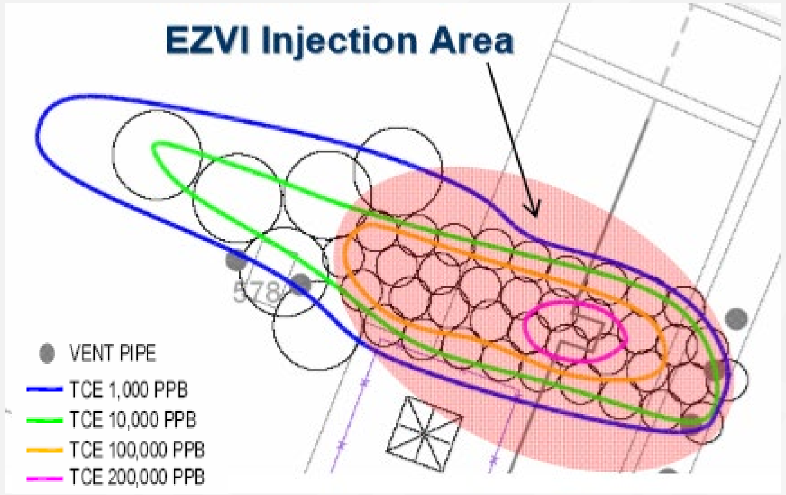
Case Study Examples

- Federal Site #1 – EZVI source destruction (TCE) with ERD in plume
- Federal Site #2 – EZVI source destruction (TCE) with ERD in plume

Case Studies – Federal Site #1

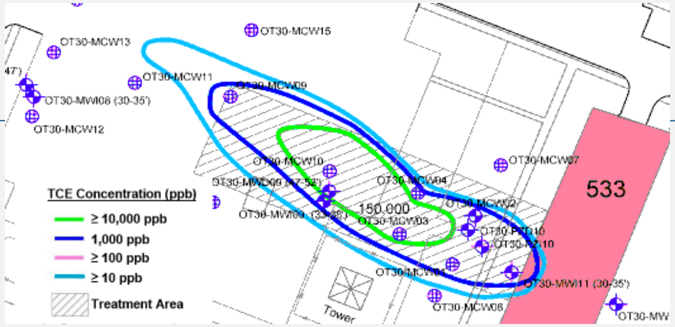
- Source Area - 75 ft x 150 ft x 40 ft (vertical)
  - Targeted GW TCE conc's > 100 ppm
- Dissolved Plume - 20 acres
  - Targeted GW TCE conc's between 10 – 100 ppm
- Source Zone Treatment - 62,000 gallons of 10% EZVI
  - Targeted 25% of effective pore volume
- Plume Treatment – Electron Donor & Bioaugmentation
- Injection Method – Pneumatic Fracture with injection



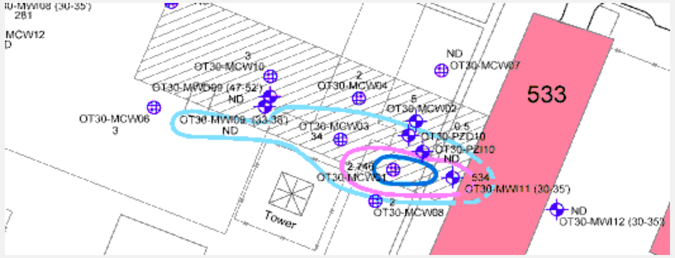


RITS Spring 2009: EZVI Treatment of Chlorinated Solvents

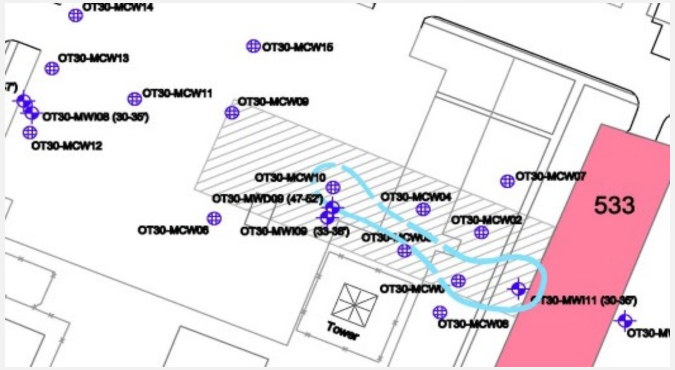
Case Study – Federal Site #1



Baseline



3 yrs Post EZVI Injection

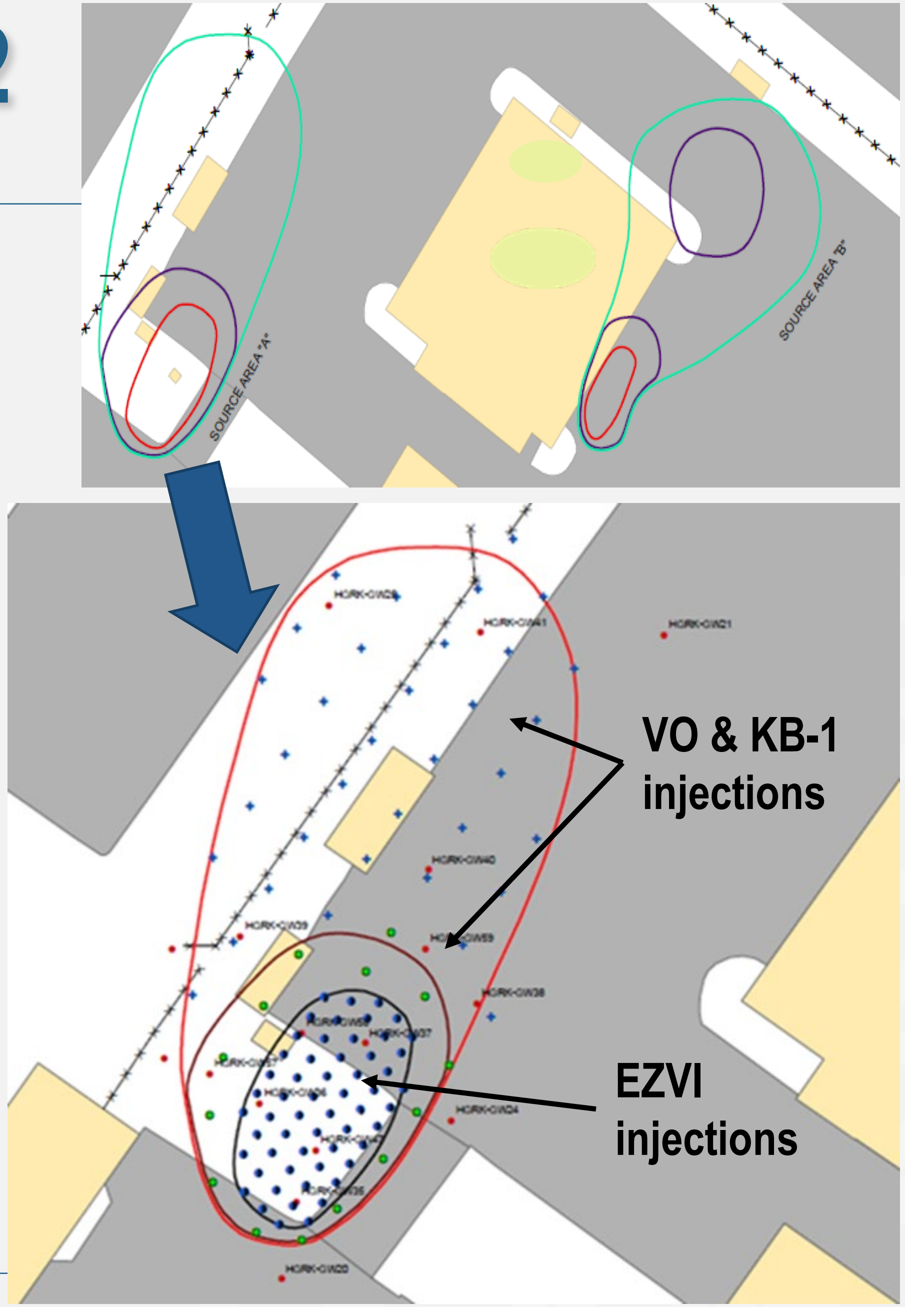


4 yrs Post EZVI Injection

- Baseline GW samples TCE up to 350 ppm
  - 1 YR = 89% destruction of source area TCE
  - 4 YRs = 94% destruction of source area TCE
  - 7 YRs = 99% destruction of source area TCE
- **One EZVI injection event**
- Prior to EZVI injection-
  - Estimated to take ~ 280 yrs. to remediate site via MNA
- Post EZVI injection-
  - Estimated to attain remediation goals < 60 yrs.

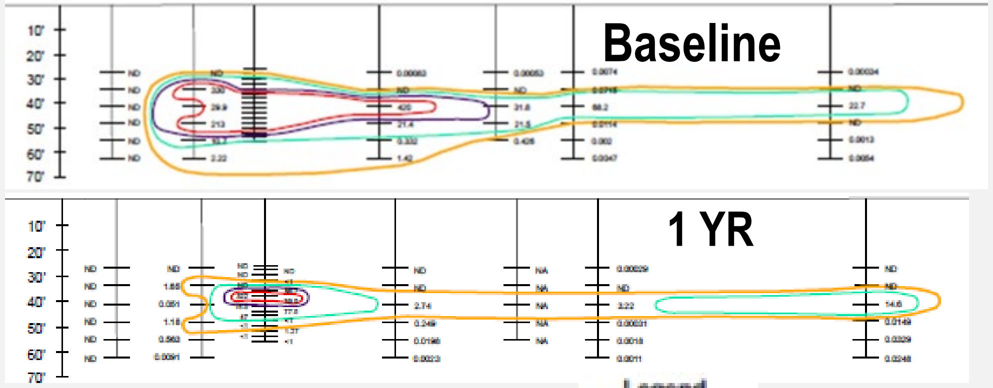
Case Study – Federal Site #2

- **DNAPL Area “A”** – 50 ft. x 100 ft. x 40 ft. (vert)
  - ➢ Targeted GW TCE conc’s > 200 ppm
- **DNAPL Area “B”** – 20 ft. x 60 ft. x 40 ft. (vert)
  - ➢ Targeted GW TCE conc’s > 200 ppm
- **Source Zone Treatment** – 37,500 USG 10% EZVI
  - ➢ Area A – Dosed at 6% of effective pore volume
  - ➢ Area B – Dosed at 10% of effective pore volume
- **Plume Treatment** – Electron Donor & Dhc
- **Injection Method** – Hybrid DPT system (Badger)

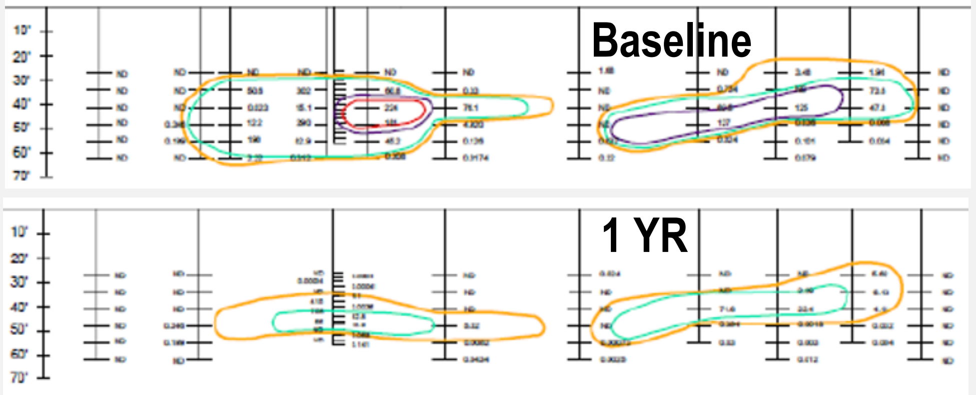


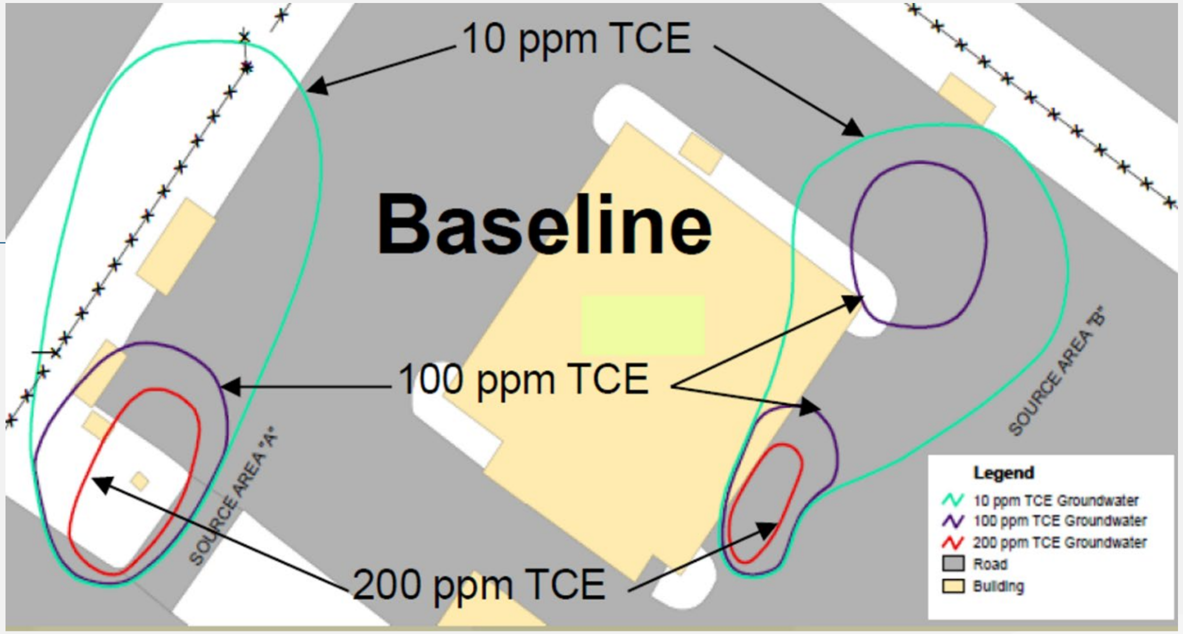
Case Study – Federal Site #2

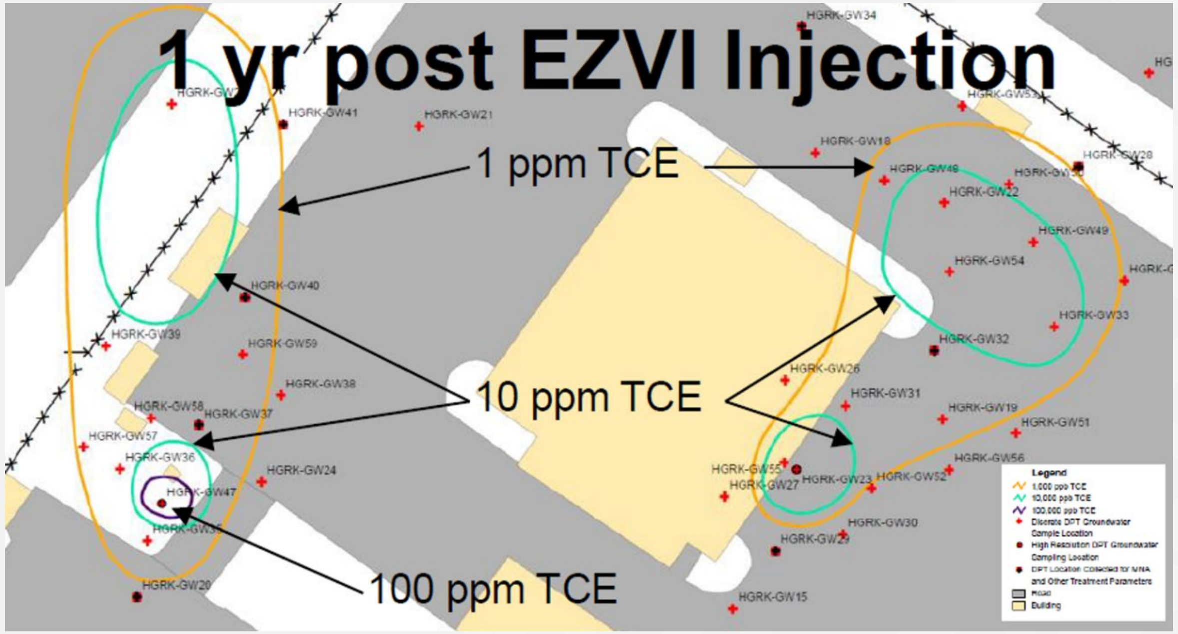
Source Area A



Source Area B







Implementation – Lessons Learned

- **<u>Dosage:</u>**
  - ➢ Early projects targeted **25%** of effective soil pore space
  - ➢ Recent projects target **<u>10%</u>** of effective soil pore space (typically)
    - ➢ Conditions to adjust dosage
      - ➢ soil type and implementation method
      - ➢ free phase DNAPL and <u>Vadose soils</u> (~ 15%)
- **<u>Formulation:</u>**
  - ➢ Original formula included ZVI at 17% (w/w)
  - ➢ Current typical formulation contains ZVI at 10% (w/w)
  - ➢ Original formula used for high concentration and low permeability sites
- **<u>ZVI:</u>**
  - ➢ Original formulation used nano ZVI
  - ➢ Current typically use small micron ZVI (< 5 μm)

<u>Handling & Storage:</u>

- ➢ Early projects utilized large tanks for on site storage (6,000 USG tanks)
- ➢ Recent projects utilize IBC totes or tanker trucks with recirculation pumping for large projects (> 20,000 USG)

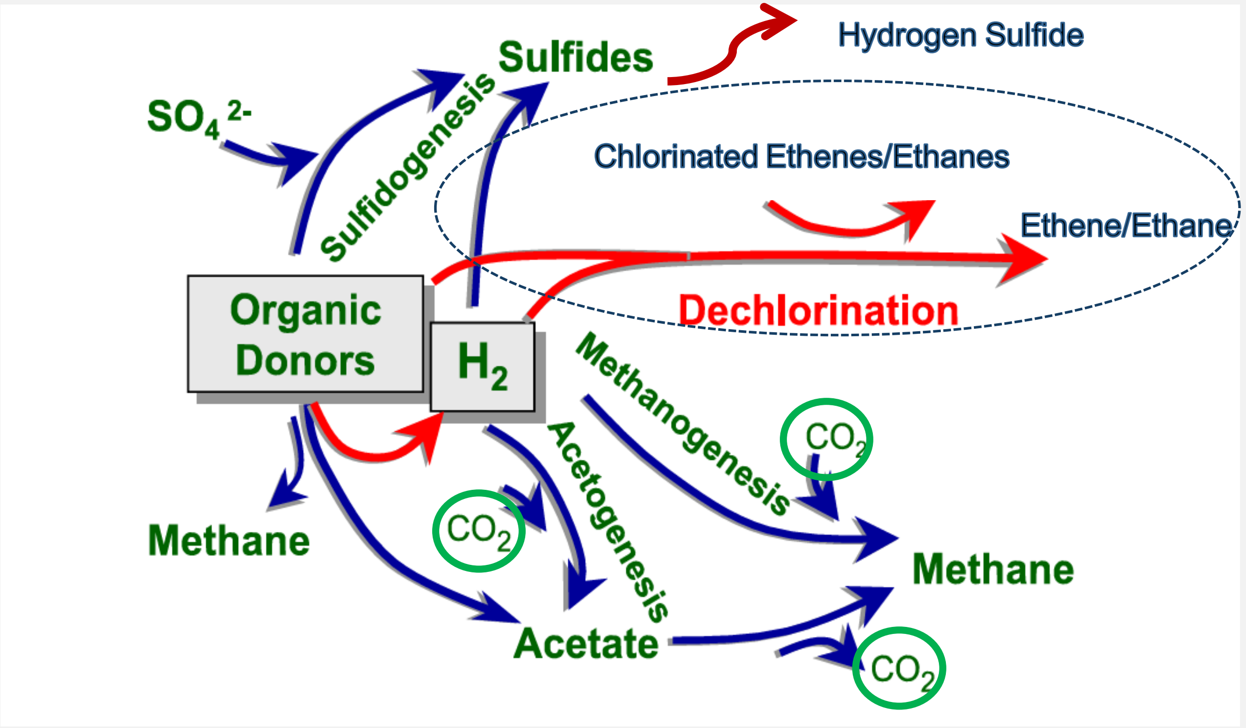
Recent Advancements to the EZVI Technology

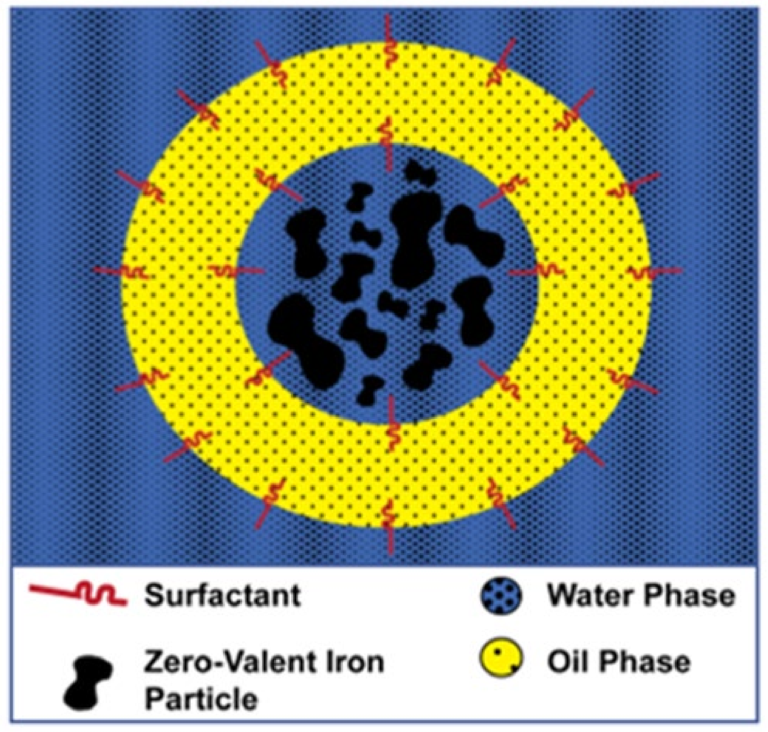
- **Optimization of Biotic Processes**
  - Controlled methanogenesis
- **Optimization of Abiotic Processes**
  - Catalyzed ZVI

Recent Advancements

Optimization of Biotic Processes

- Methanogens dominate anaerobic ecosystems and they can hinder dechlorination by competing with dechlorinating bacteria for available H_2 (Yang and McCarty, 1998).

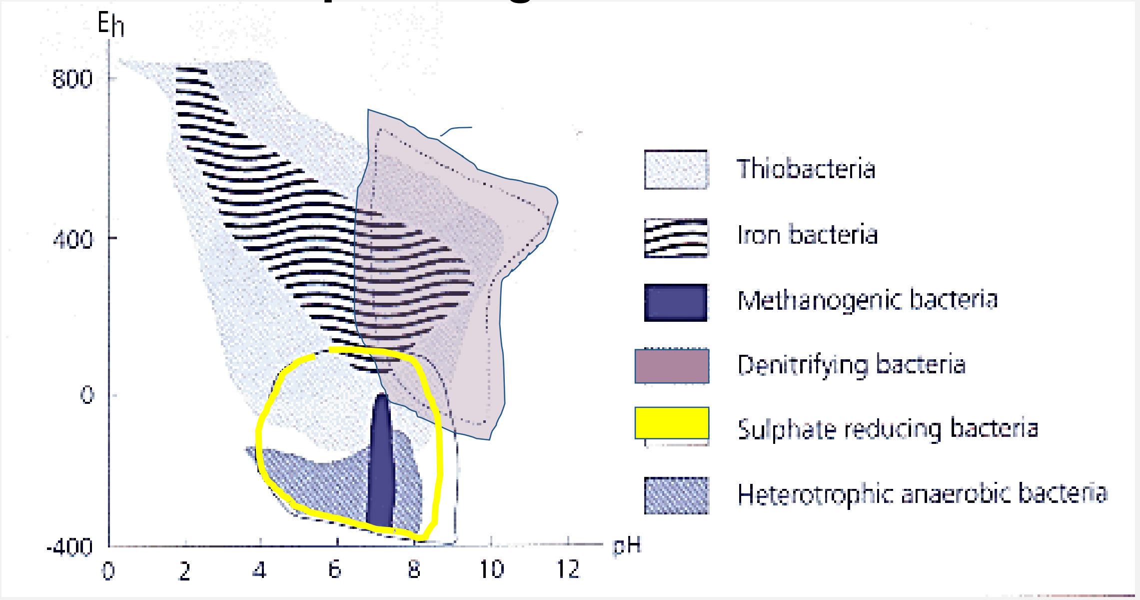




Recent Advancements
Optimization of Biotic Processes

Microbe	Doubling Times
Dehalococcoides spp.	24 to 48 hours
Methanogens with cytochromes	10 hours
Methanogens without cytochromes	1 hour

Idealized Eh pH Ranges for Microbial Growth



What is the problem with methanogens?

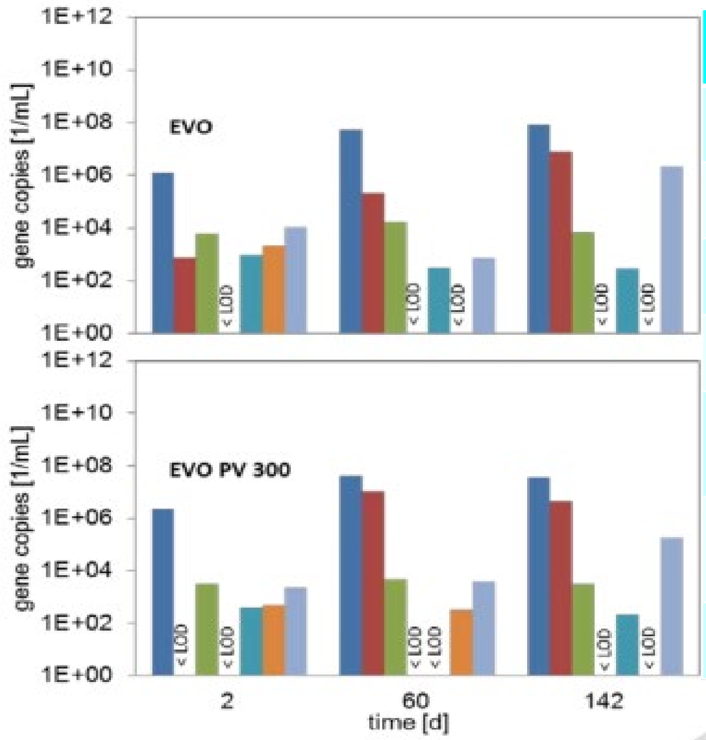
- Even in a highly oxidized setting with relatively high total concentrations of PCE and TCE, generating just 20 mg/L of methane constitutes **greater than 33%** of the total amendment consumption based on moles of H_2.

Constituent	Groundwater Concentration (mg/L)	Molecular Weight (g/mol)	Moles of H_2 to Reduce Mole Analyte	Moles of H_2 Acceptor In Treatment Area
Contaminant Electron Acceptors (To End Product Ethene)				
Tetrachloroethene (PCE)	10.0	165.8	4	1,393
Trichloroethene (TCE)	7.0	131.4	3	364
cis-1,2-Dichloroethene (cDCE)	0.0	96.9	2	0
Vinyl Chloride (VC)	0.0	62.5	1	0
Complete Dechlorination (Soil+Groundwater) Subtotal				1,757
Native Electron Acceptors				
Dissolved Oxygen	9.0	32	2	199
Nitrate (as Nitrogen)	9.0	62	3	682
Sulfate	50.0	96.1	4	736
Fe^{+2} Formation from Fe^{+3}	20.0	55.8	0.5	63
Mn^{+2} Formation from Mn^{+4}	10.0	54.9	1	64
Baseline Geochemistry Subtotal				1,745
Hydrogen Waste for Methane Formation				
Methane Formed	20.0	16	4	1,769
Initial Treatment Area Hydrogen Usage				5,271

Recent Advancements – Controlled Methane

How can methanogens be controlled?

- Genetically unique – ***Archaea***
- Target Methanogens - using naturally occurring statins (RYR Extract) and select essential oils/saponins to disrupt enzyme and coenzyme processes unique to methanogens



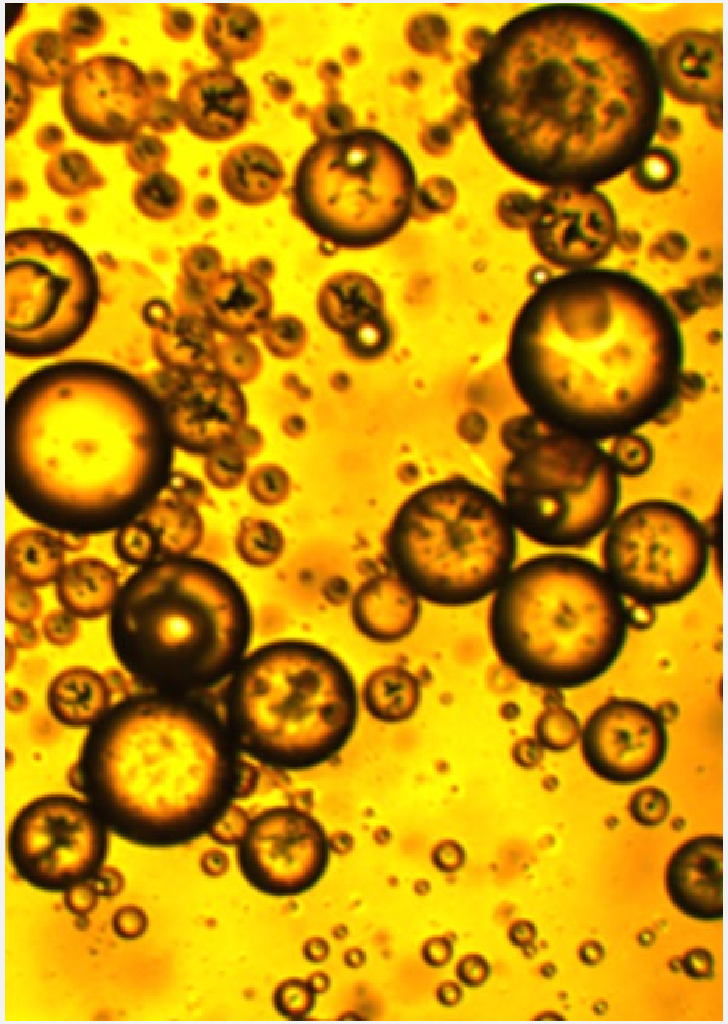
CH4	EVO	PV600
mg/L	2.75	0.09
umol	145	15
ppmv	1,450	150
mcrA	**2E6**	**1E2**
DHC dco	**5E6**	**3E6**
DHB deha	**1E3**	**6E3**
Day 142		

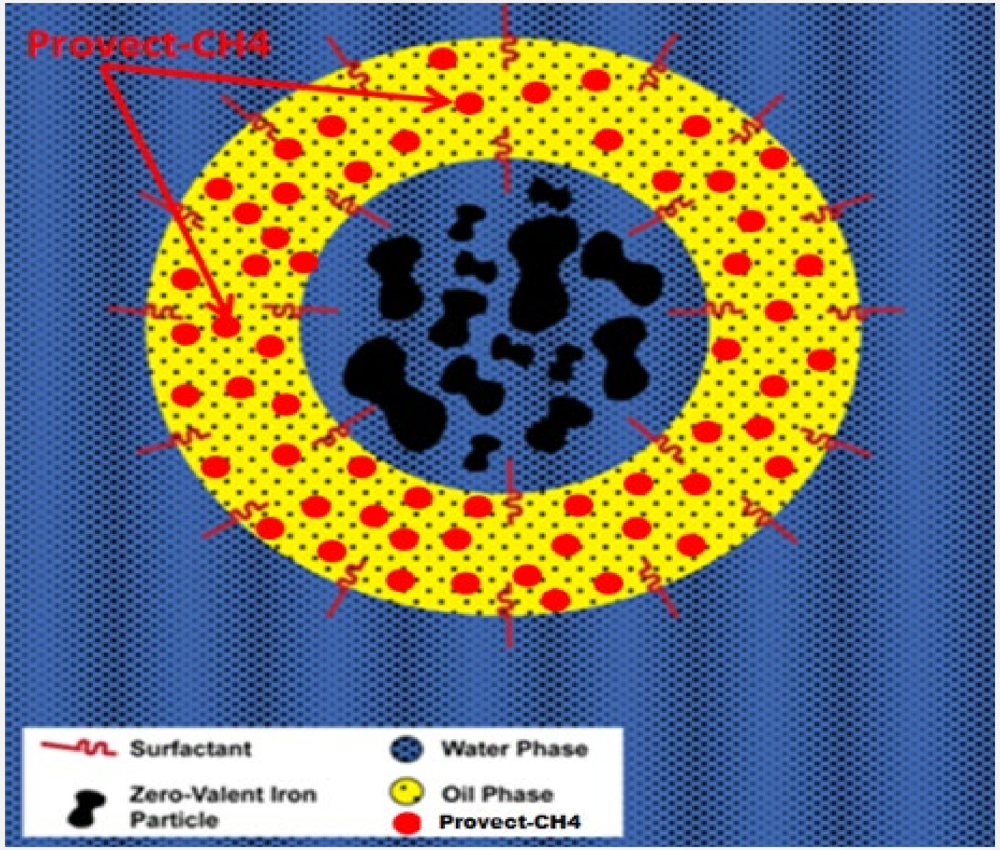
2 60 142
time [d]

Figure 5-7: qPCR results for the microcosms EVO with and without Provect-CH4™ (limit of detection (LOD) = 10 copies/mL)

qPCR data from Provectus

Recent Advancements – Controlled Methane





Benefit: in situ DNAPL destruction with controlled methanogenesis

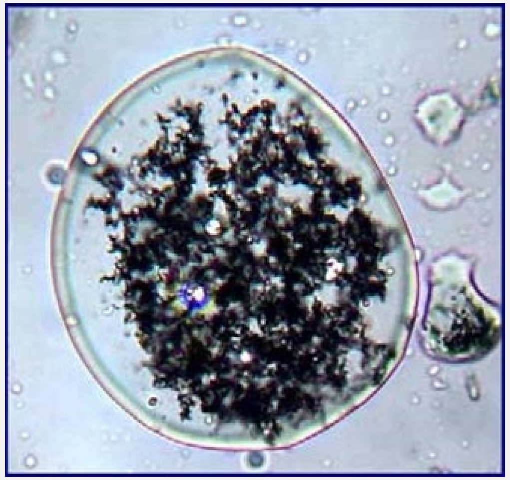
Recent Advancements
Optimization of Abiotic Processes

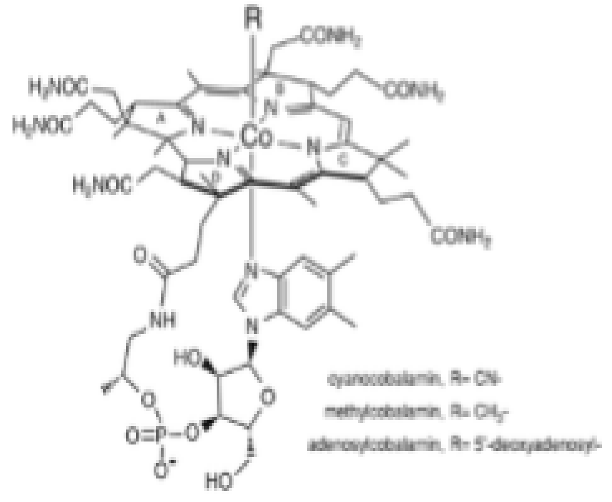
Optimizing abiotic processes within the <u>interior of the emulsion</u>

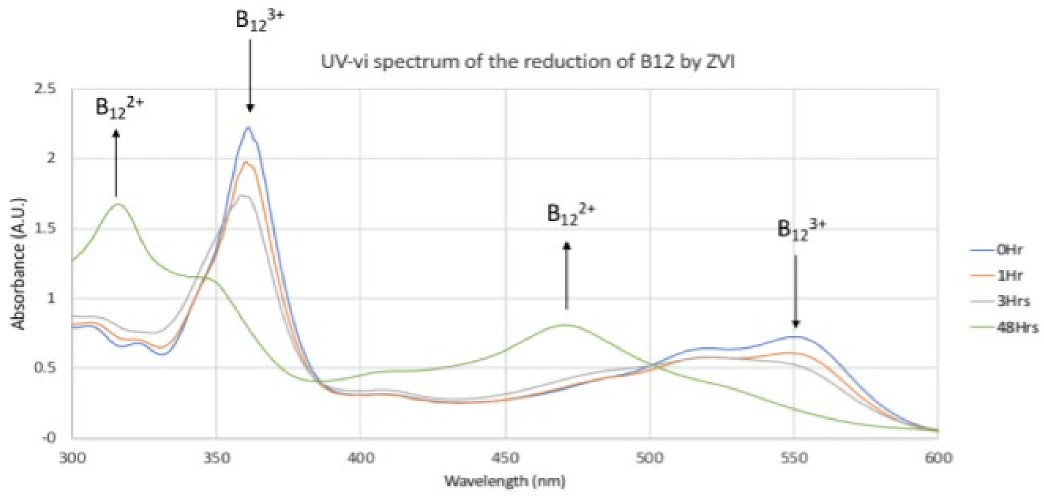
- **Reactivity:**
  - ➢ Catalyzing ZVI electron transfer processes

Vitamin B12 (cobalamin)

- ➢ Naturally occurring organometallic compound
- ➢ Naturally occurring electron mediator
- ➢ Water soluble & non toxic
- ➢ Contains Co in center of corrin ring structure
- ➢ B12 must be in a reduced state to transfer electrons



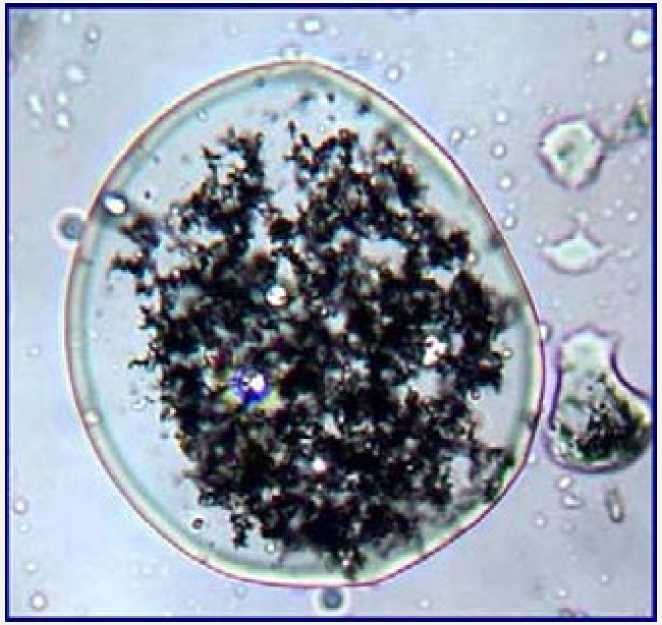


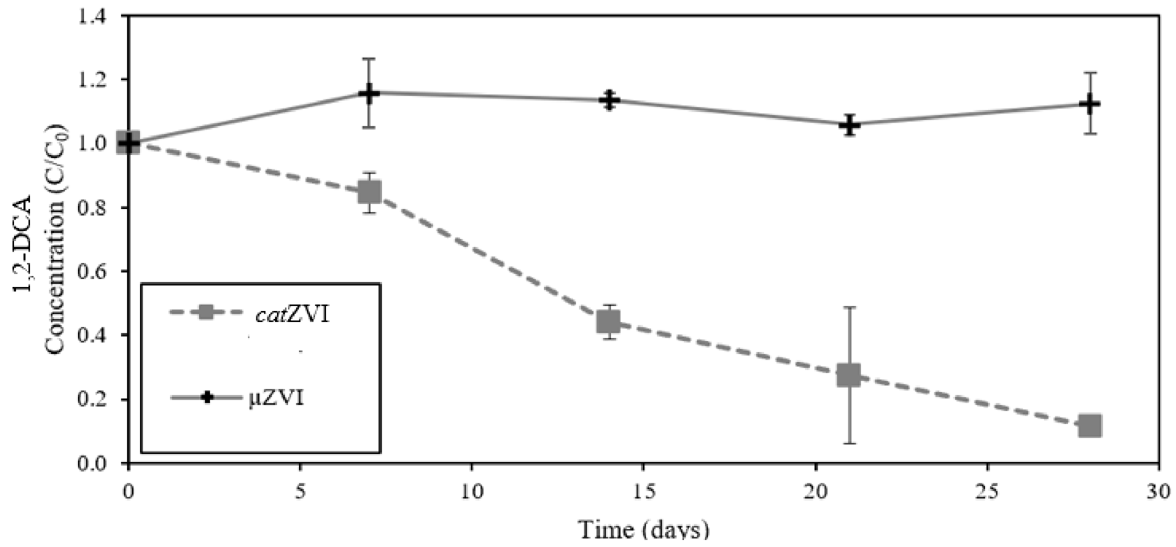


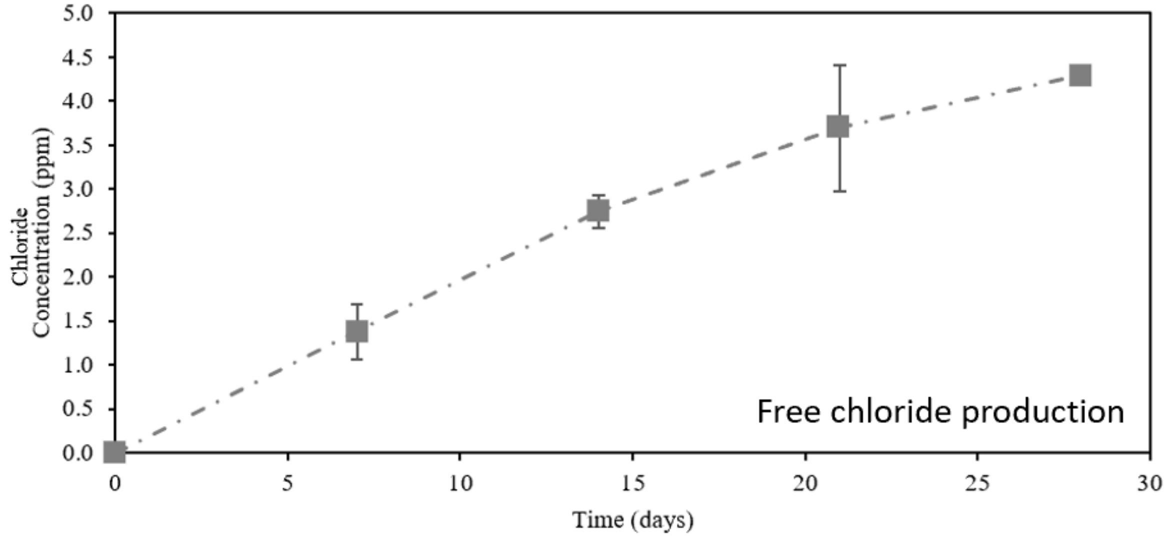
Recent Advancements – Catalyzed ZVI

Optimizing abiotic processes

- **Reactivity:**
  - Electron transfer processes
    - 1,2 – Dichloroethane (1,2 – DCA)





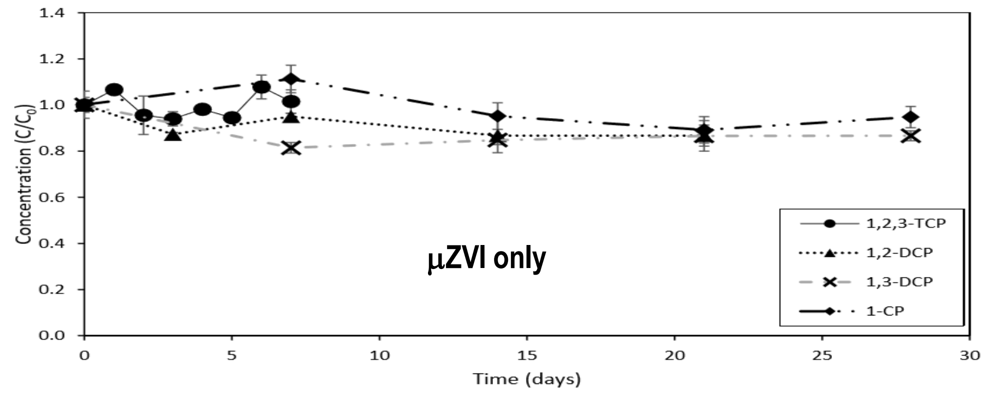


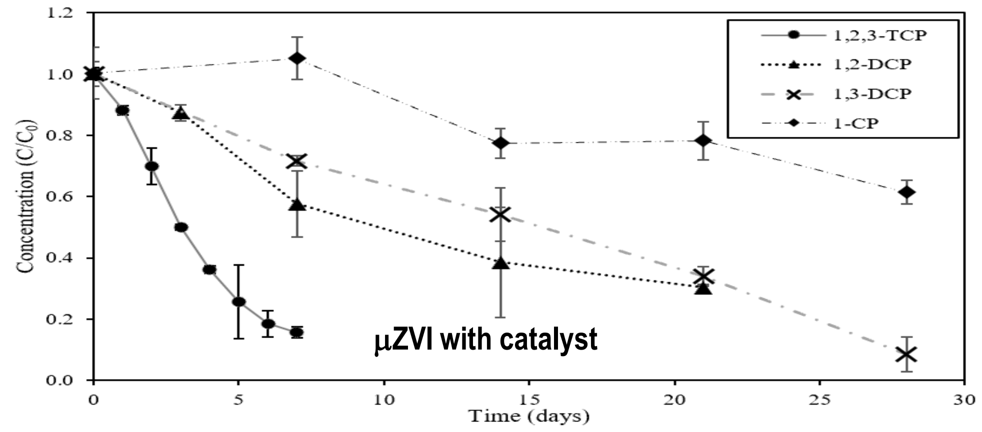
Recent Advancements
Catalyzed ZVI

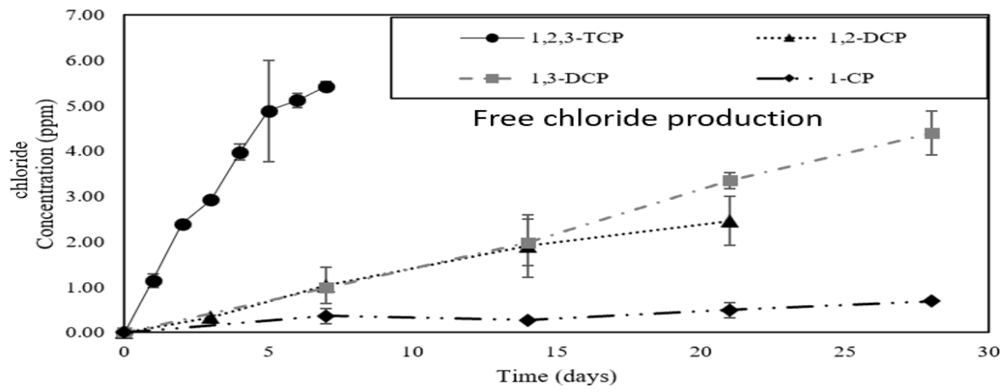
<u>Optimizing abiotic processes within the interior of the emulsion</u>

<u>Compounds Tested</u>

- 1,2,3 – Trichloropropane (1,2,3 – TCP)
- 1,2 – Dichloropropane (1,2 – DCP)
- 1,3 – Dichloropropane (1,3 – DCP)
- 1 – Chloropropane (1 – CP)



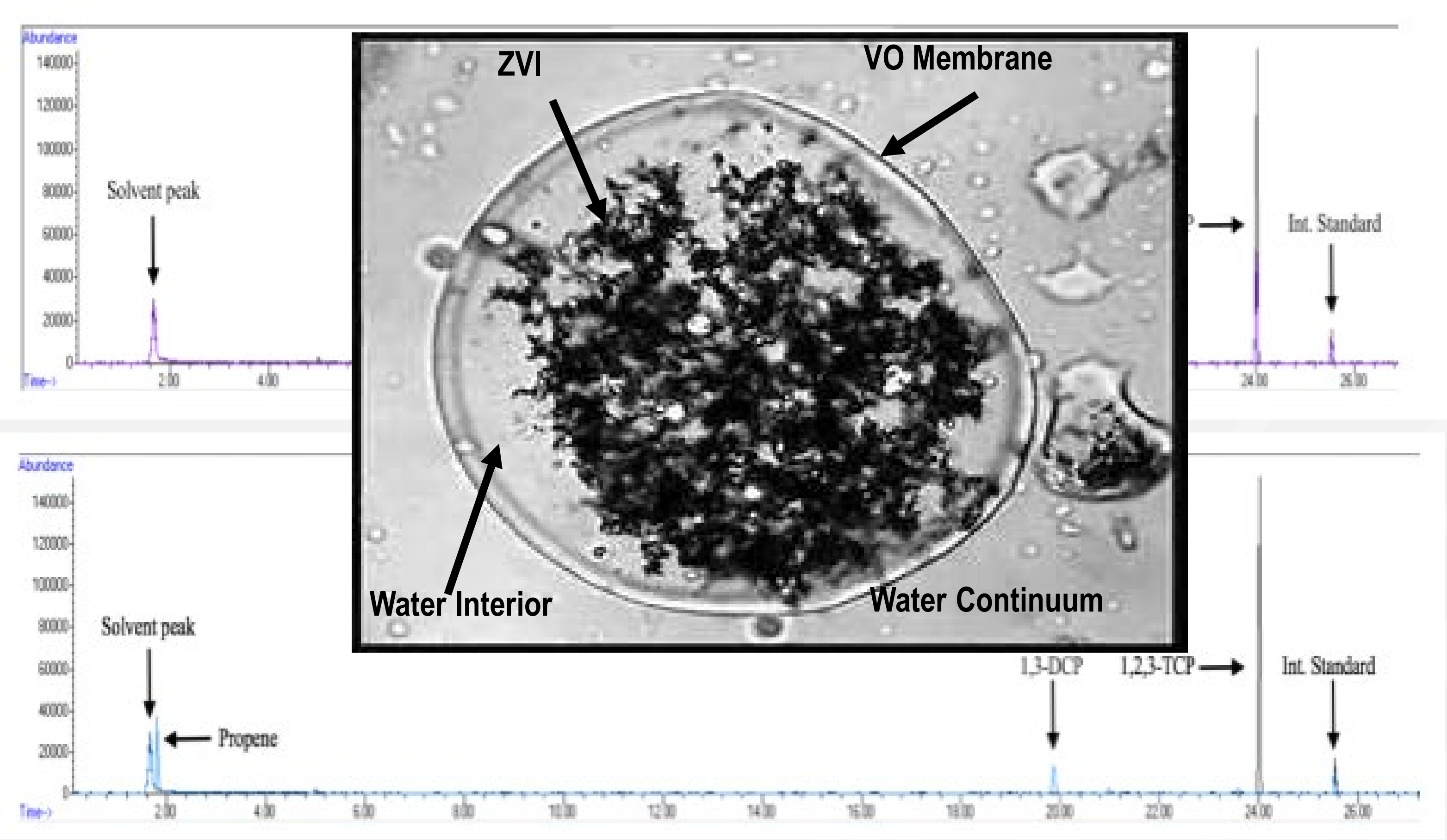




<u>Benefit: *Expanded Range of Catalysis*</u>

Recent Advancements
Catalyzed EZVI

Optimizing abiotic processes within the interior of the EZVI emulsion



Compounds Tested

- 1,2,3 – Trichloropropane (1,2,3 – TCP)

Benefit: *Expanded Range of Catalysis*

Summary – DNAPL destruction with EZVI

- Contaminant Reduction & EZVI Longevity
  - Typical source area parent VOC concentration reduction of ~ 90% within < 1 year
  - EZVI has been shown to be effective in the subsurface for >5 years
- Source Area Effects
  - Directly destroys source material
  - Significantly reduces mass flux
- Plume Effects
  - Adjacent to source area: Fermentation reactions provide hydrogen for biotic transformations or "polishing" adjacent to injection area
  - Downgradient: Eliminates on-going source for downgradient areas
- Recent Advancements
  - Provide optimized abiotic and biotic capabilities and expand the scope of treatable contaminants
- Estimated Costs
  - For product and DPT injections approximately **= $121.66 - $155.08/yd^3 of DNAPL impacted soil**

Thank You!

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Recent Advancements – Controlled Methane

REMEDIATION Summer 2016

Managing Excessive Methanogenesis During ERD/ISCR Remedial Action

Jim Mueller

J. Greg Booth

WOODARD &CURRAN

Recent Advancements
Catalyzed ZVI

Optimizing Abiotic Processes within the interior of the emulsion

Hindawi
Journal of Chemistry
Volume 2019, Article ID 7565464, 8 pages
https://doi.org/10.1155/2019/7565464

Hindawi

Research Article

Remediation of Chlorinated Alkanes by Vitamin B_{12} and Zero-Valent Iron

Nicole Lapeyrouse,[1] Muqiong Liu,[1] Shengli Zou,[1] Greg Booth,[2] and Cherie L. Yestrebsky[1]