



REGENESIS[®]

**Employing Synergistic Colloidal
Technologies to Degrade DNAPL**

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REGENESIS

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Overview

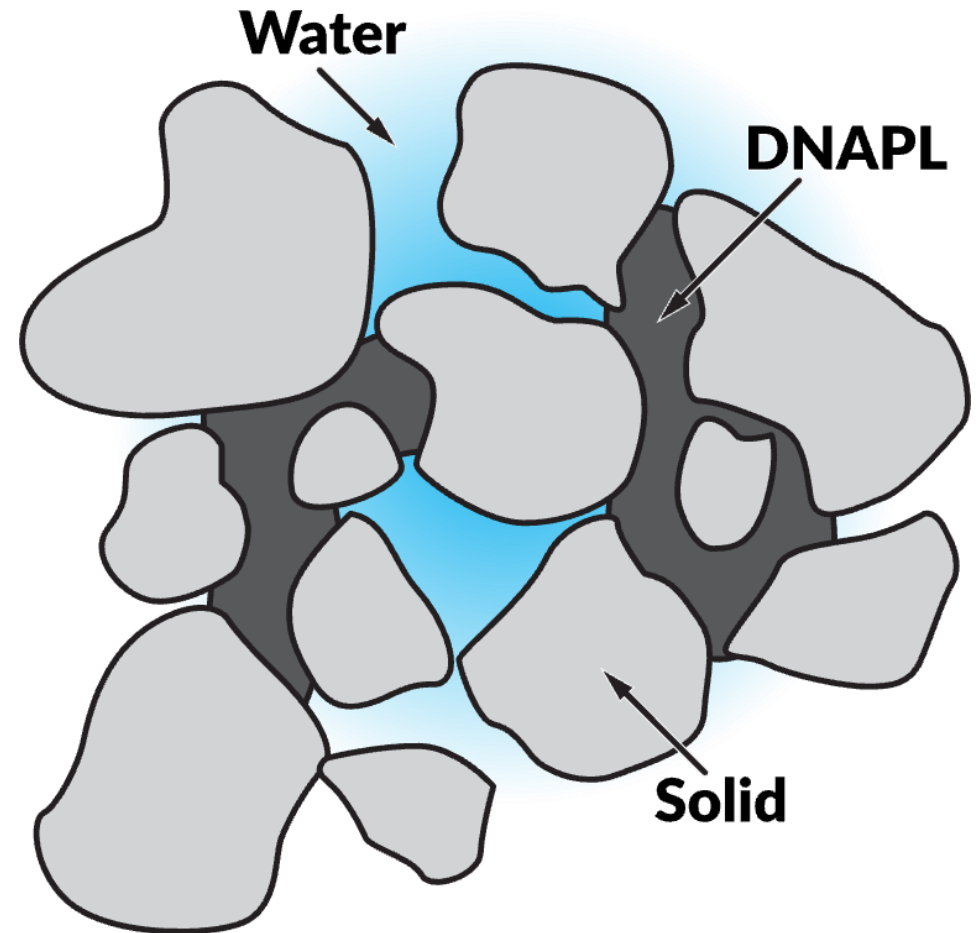
- Source Zone Characteristics
- Using Emulsions to Partition and Solubilize DNAPL
- ZVI Enhanced Bioremediation
- Application Example



Source Zone and DNAPL Characteristics

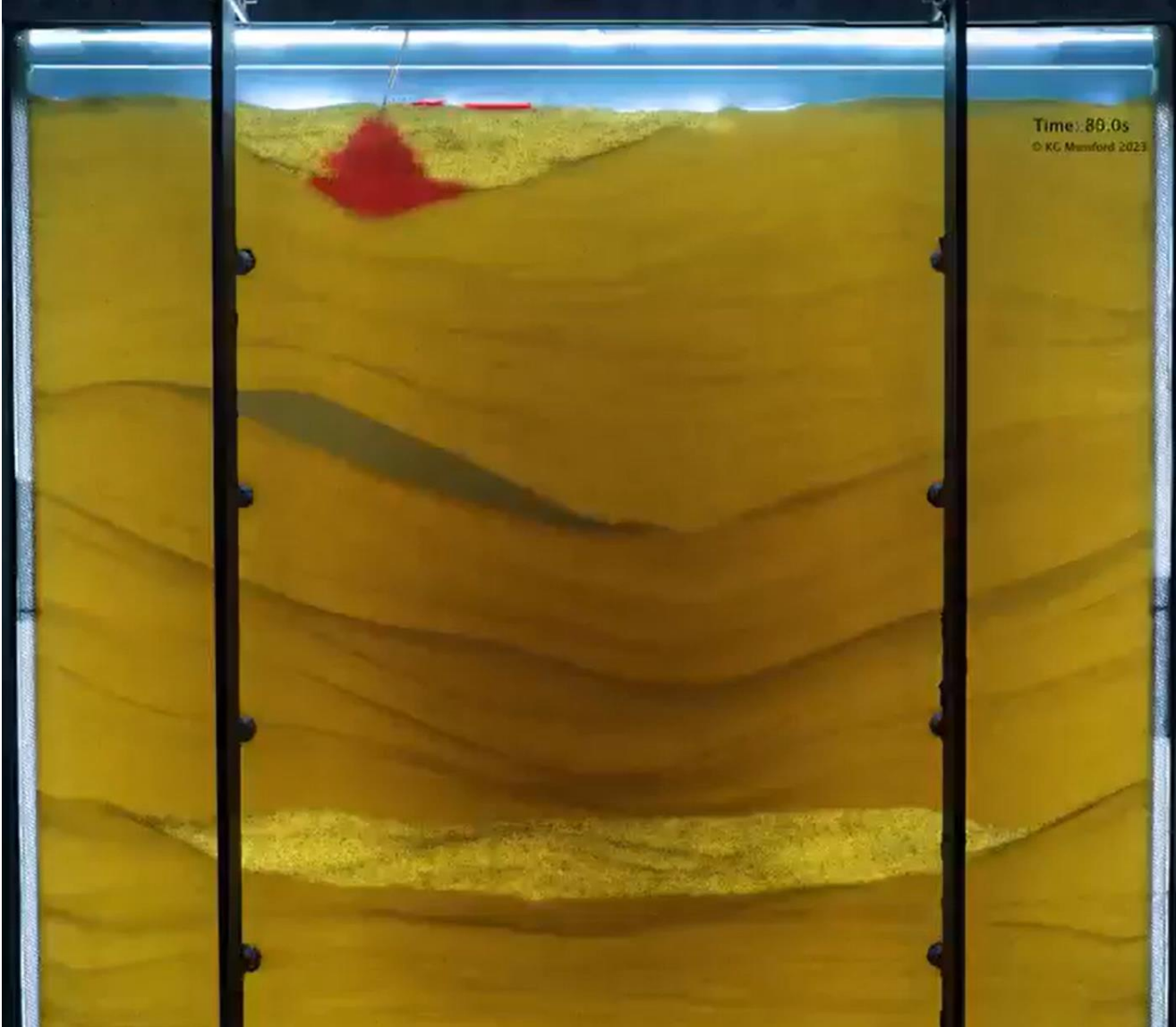
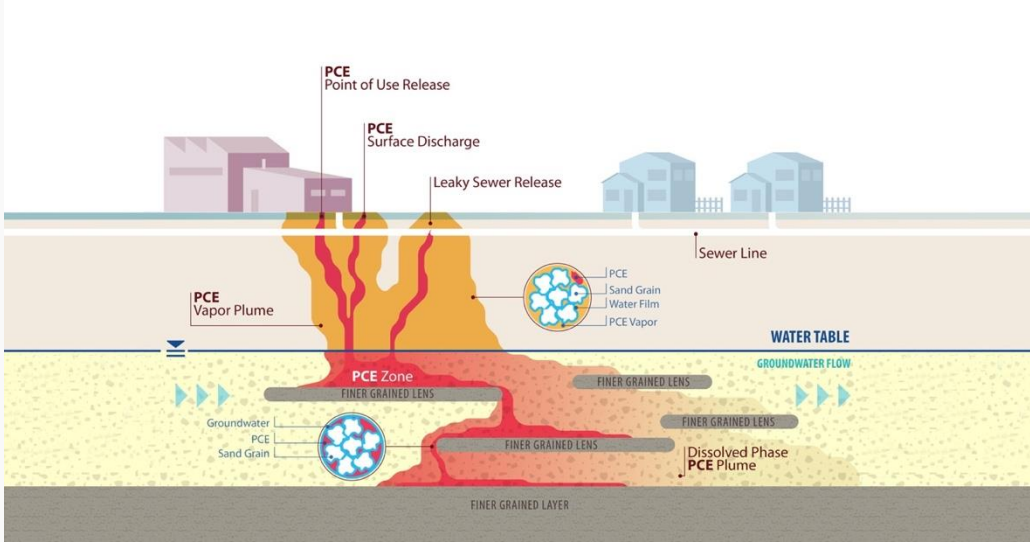
DNAPL Characteristics

- DNAPL compounds have low aqueous phase solubility
 - PCE ~150 mg/L; TCE ~1000 mg/L
- DNAPL migrates into soil porosity, and is not easily dislodged
- DNAPL can persist for decades



Chlorinated Solvents

Dense Non-Aqueous Phase Liquids (DNAPLs)



CPT Video Cone Footage - Weathered Chalk PCE DNAPL



Current Common Remediation Options

Remedial Options: Physical

Pump and Treat

- Slow, and can be expensive

Thermal Treatments

- Usually effective, \$\$\$, can require polishing

Excavation

- Effective with depth and infrastructure limitations



Remedial Options: Chemical/Bio

Chemical Oxidation

- Persulfate or permanganate



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Aerobic Biodegradation

- Calcium peroxide or sparging



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Anaerobic Bioremediation

- Sodium lactate/molasses



Remedial Options: Chemical/Bio

Chemical Oxidation

- Persulfate or permanganate

Aerobic Biodegradation

- Calcium peroxide or sparging

Zero Valent Iron/Biogeochemical

Anaerobic Bioremediation

- Sodium lactate/molasses

Operate best in dissolved
phase contaminants

A background photograph of a remediation site. In the foreground, a large piece of machinery, likely a drilling rig, is positioned on a dirt surface. Two workers wearing orange safety vests and hard hats are standing near the rig. The background shows a clear blue sky, utility poles, and some industrial buildings or containers. The overall scene is a typical remediation site during an active operation.

Alternative Solution: Using Emulsions to Partition and Solubilize DNAPL

Biological Treatment Using Emulsions and Zero Valent Iron

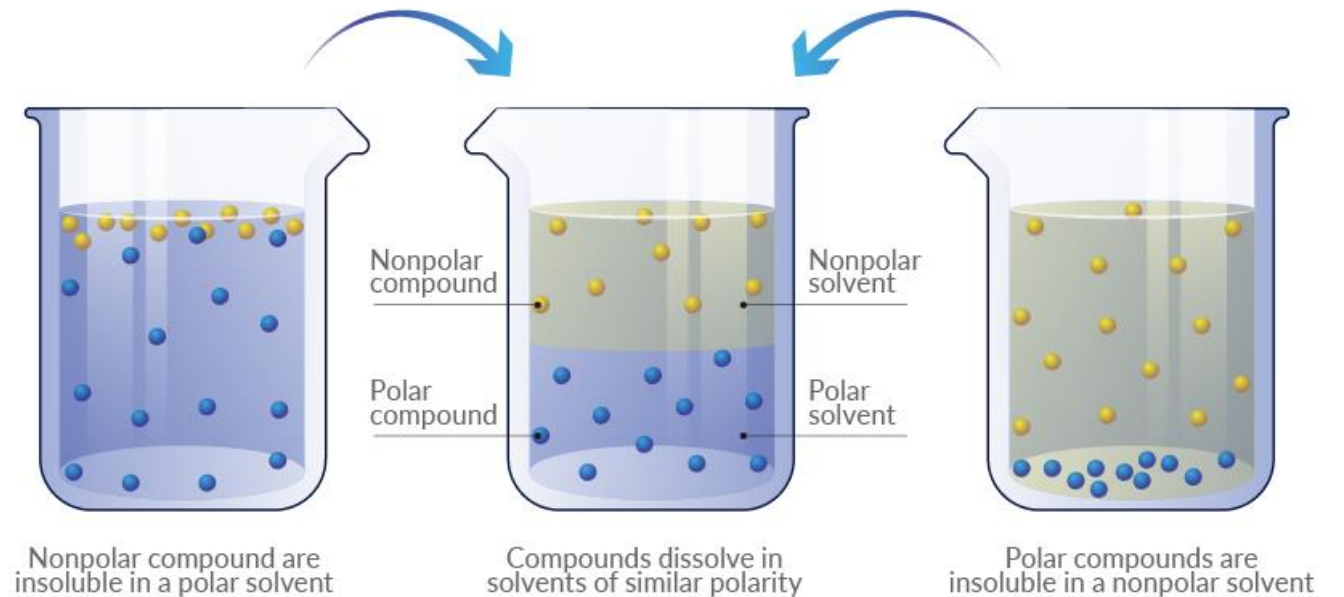
Co-apply a dilute mixture of:

- Oil-in-water emulsion such as 3DME
- Sulfidated microZero valent iron (S-mZVI)
- Dechlorinating microbes
- Optionally, nutrients, pH modifiers, vitamin B12
- Water



Role of Emulsion

- DNAPL globules/ganglia are hydrophobic
- ...and so are droplets of an oil emulsion
- “Like-Dissolves-Like”
- Upon contact, DNAPL is quickly partitioned into the donor emulsion



This makes electron donor emulsions ideal for source zones with DNAPL

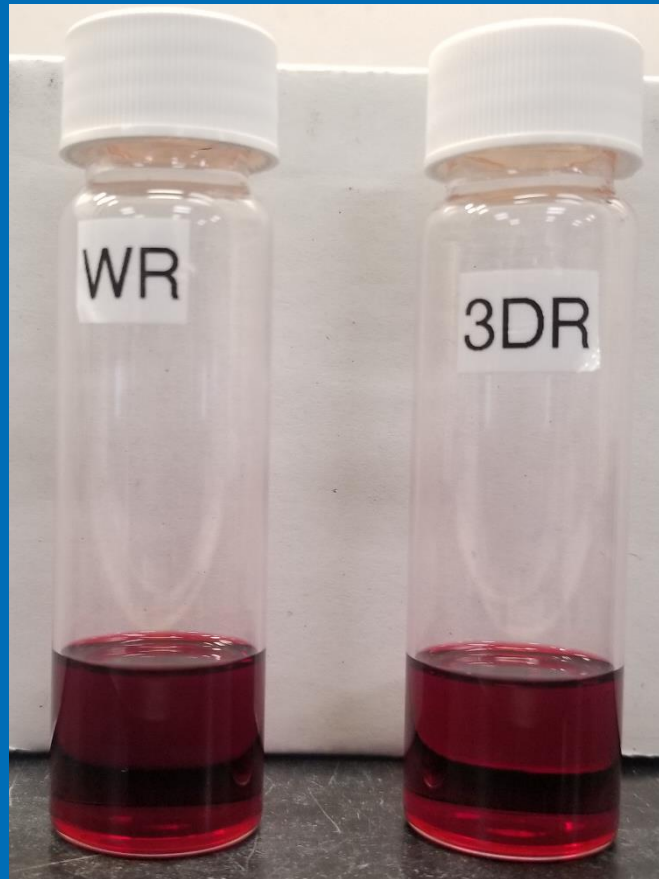
Dye Experiment

Dye Experiment

Contents:

10 g PCE

4 mg Red Dye



Contents:

10 g PCE

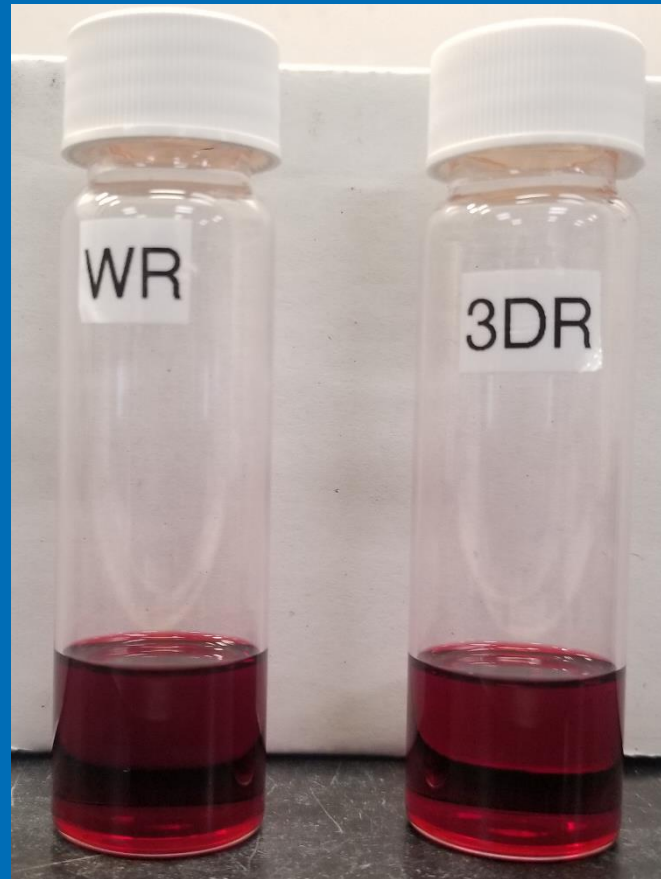
4 mg Red Dye

Dyed PCE

Dye Experiment

Contents:

10 g PCE
4 mg Red Dye
30 mL Water



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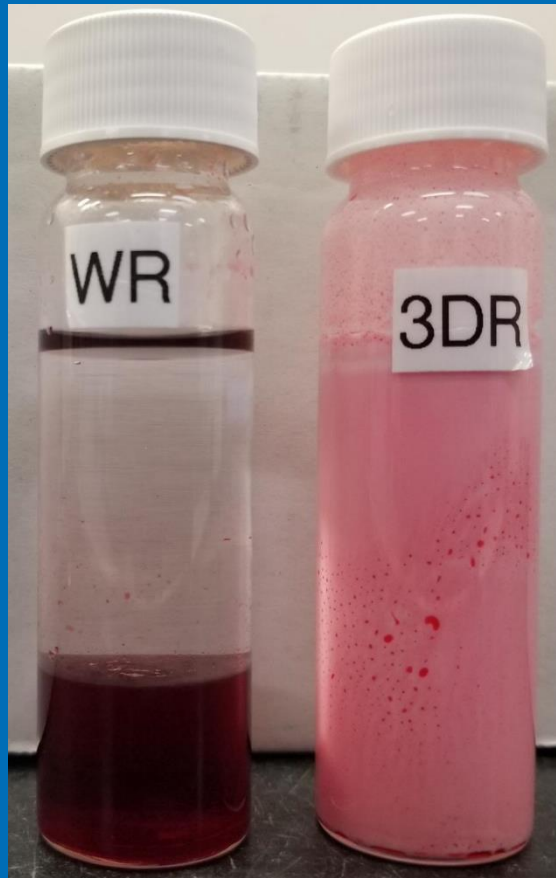
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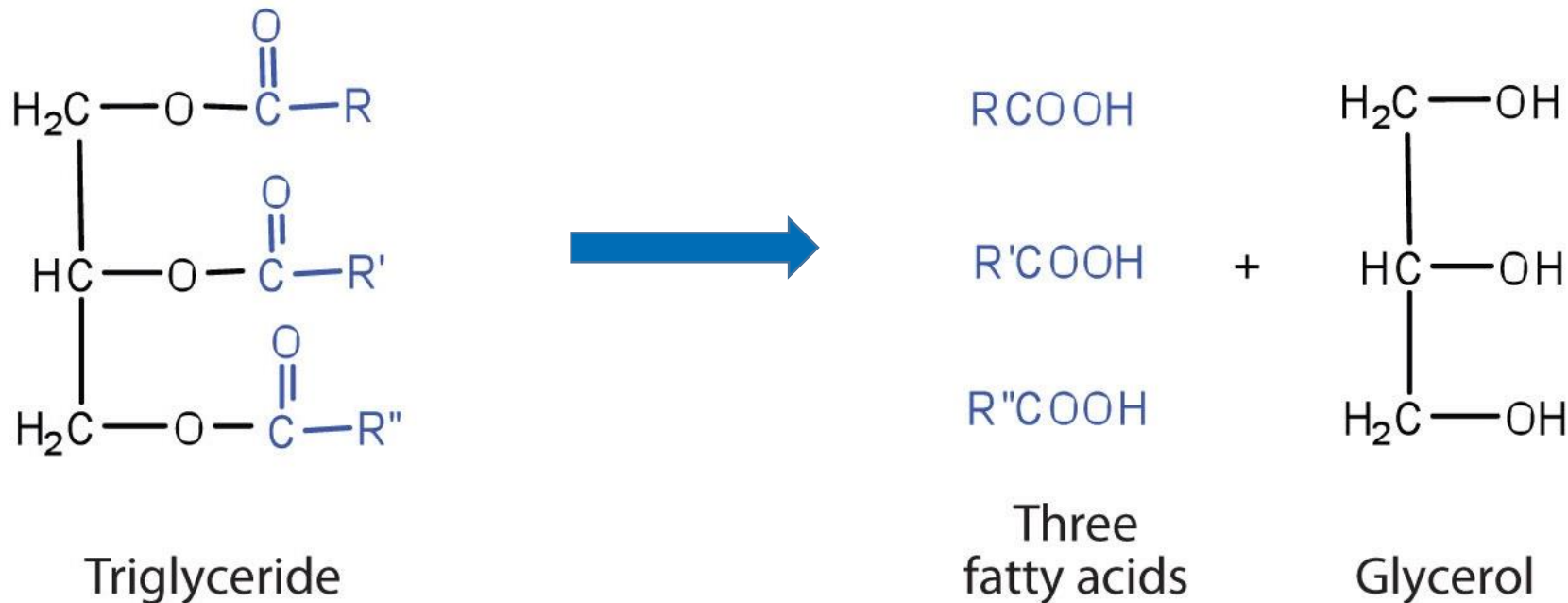
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4 mg Red Dye
30 g 3DME

Shake and Wait 1 Hour

Oil Droplet Degradation and Contaminant Release

Vegetable Oil Droplets are Biodegraded

Triglyceride ester cleavage produces a water miscible glycerol molecule and three fatty acids



Oil Droplet Degradation and Contaminant Solubilization

Volatile Fatty Acids are Biodegraded



Lineolic acid



VFA (C₁₆) + molecular hydrogen + acetic acid

Column Studies

Biological Approach: Column Study

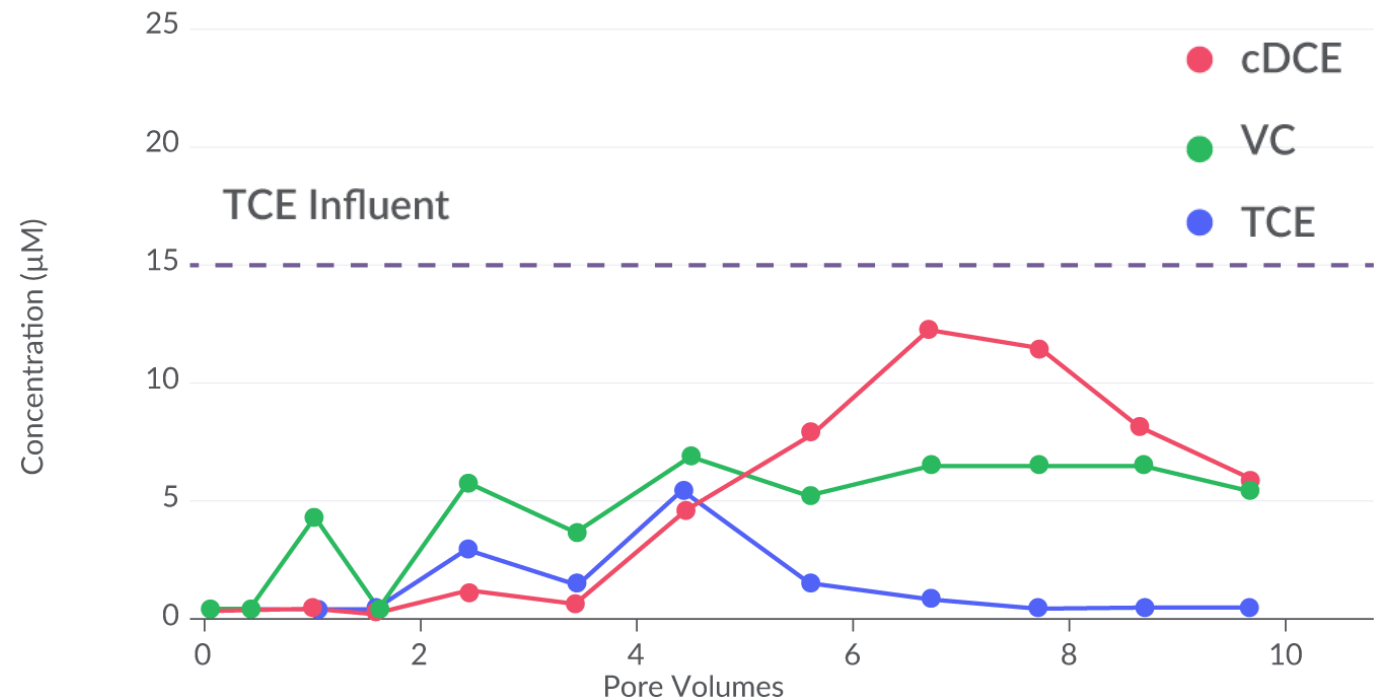
Bioremediation Only Column

- Primed with 1 g/L sodium lactate nutrients, Dhc culture
- 15 μM TCE (~ 2 mg/L) and lactate added to for 10 pore volumes at 1 pore volume per week
- Concentrations measured in effluent



Biological Approach: Column Study

- TCE Peaks at 5 μM (5 weeks)
- TCE mostly eliminated once acclimated
- At 10 weeks:
 - 6 μM cDCE
 - 6 μM VC
 - <1 μM TCE
 - ~20% molar degradation

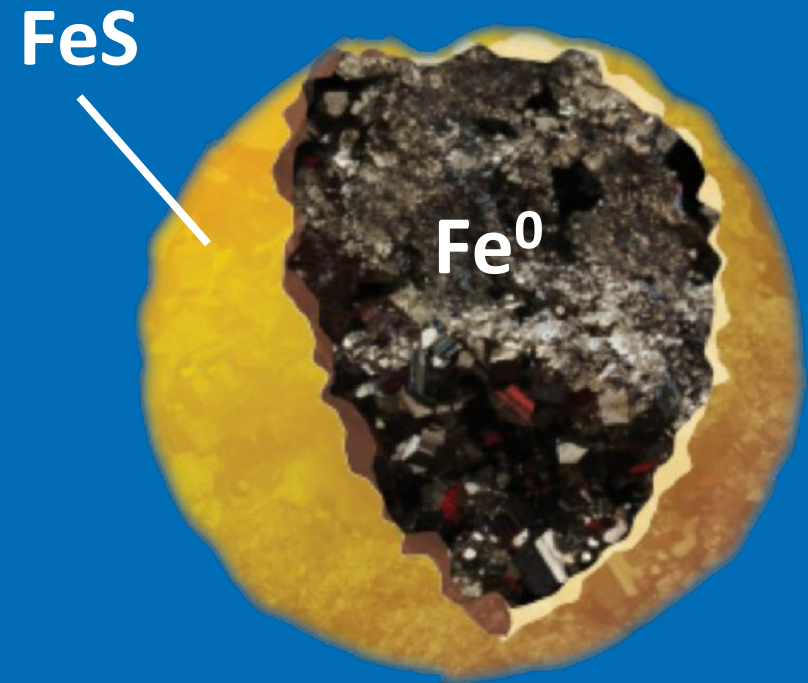


SZVI Accelerated Biodegradation

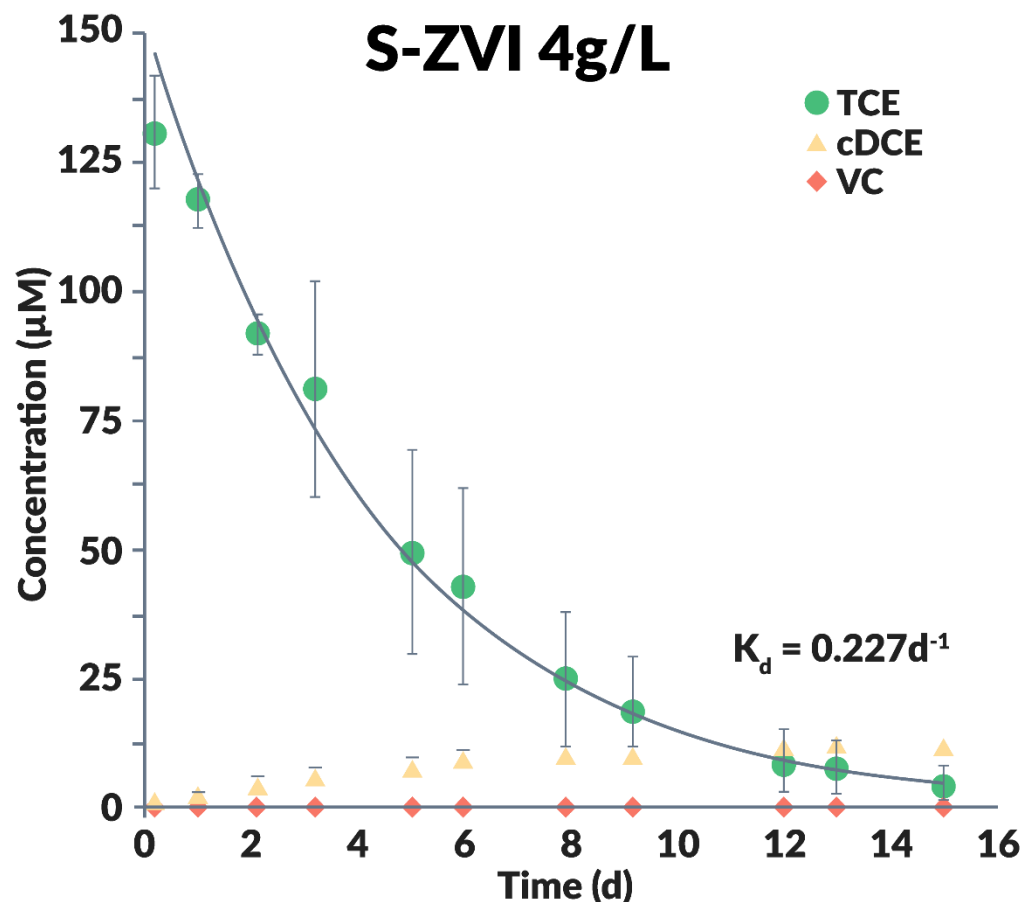
S-MicroZVI® = Sulfidated Microscale ZVI

Key Feature: Core shell microstructure

- Average diameter 2-3 microns
- Zero valent iron core ~98% mass
- Reduced iron sulfide surface (FeS) ~2% mass
- Surface layer thickness ~200 nm



S-MicroZVI Reactivity: TCE



- First order reaction kinetics
- K_{obs} : 0.227 day^{-1}
- Half life: ~ 3 days
- cDCE yield: $\sim 10\%$
- Negligible VC

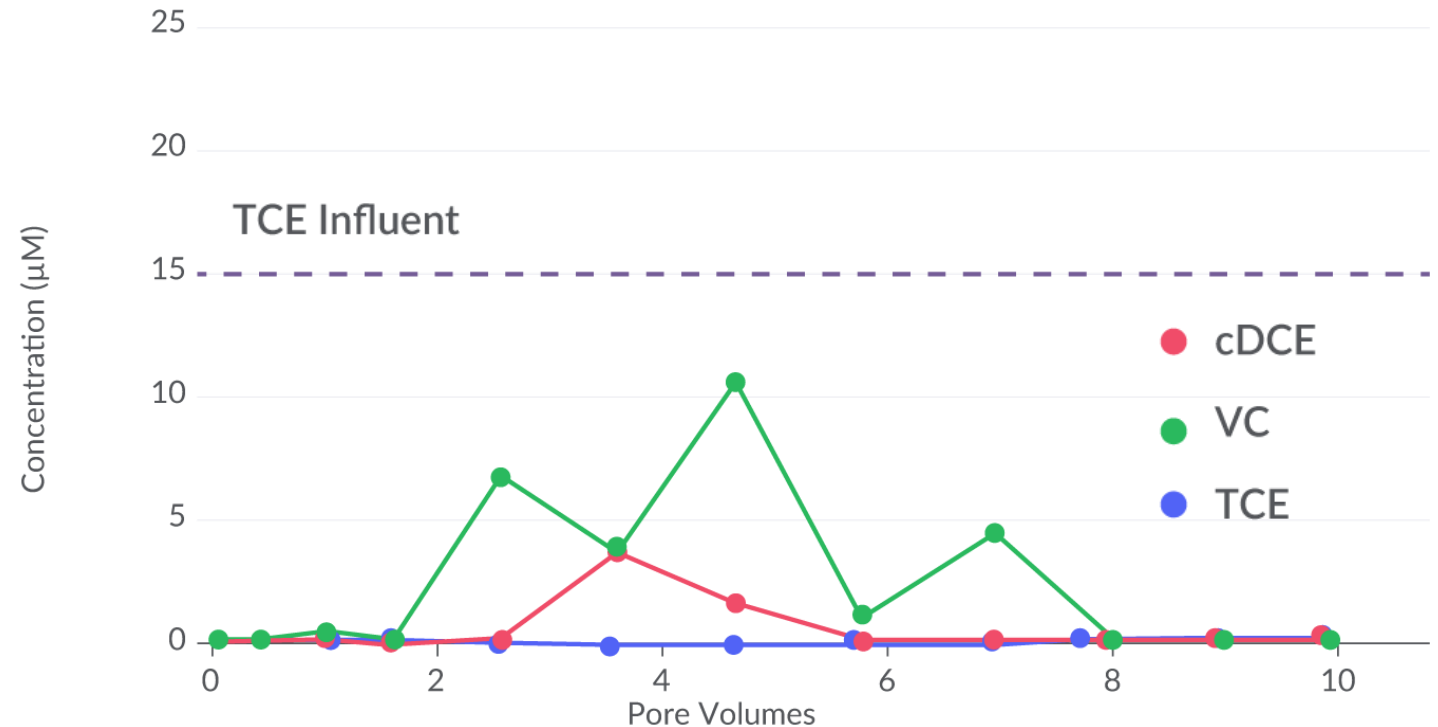
Combining Biological and Abiotic: Column Study

Same conditions as biological study
with SZVI added to column

Results

- No TCE elution at any time
- cDCE peaks at 4 μM (3 weeks)
- VC peaks at 12 μM (5 weeks)
- 100% molar degradation after 7 weeks

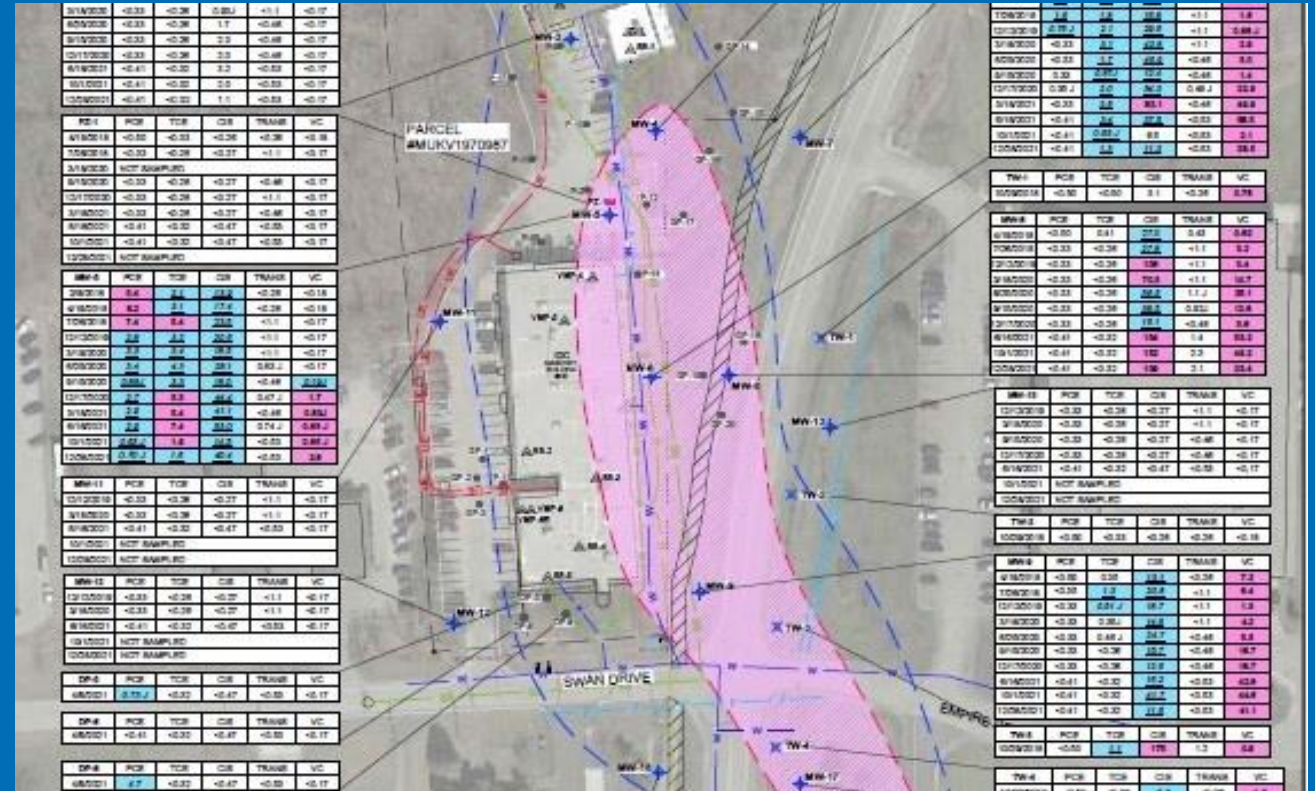
Substantial improvement compared to
biological approach



Project Case Study

SZVI Emulsion Application

- Industrial Site in Midwest
- 2800 kg 3DME
- 1700 kg S-MicroZVI
- 18 L BDI Dehalococoides
- Grid Application in Source Zone



SZVI/Emulsion Application

Monitoring Results: CVOC and Dissolved Gases

Product Application →

Date	PCE	TCE	cDCE	VC	Ethane	Ethene	Methane
Jul '18	3530	54	6	0	---	---	---
Dec '19	132	19	33	3	26	25	43
Mar '20	306	11	4	0	24	29	32
Jun '20	102	19	5000	100	34	70	189
Sep '20	0	0	9	3	126	422	7570
Dec '20	1	0	0	0	34	57	11400
Mar '21	1	0	13	4	15	16	2740
Jun '21	1	0	0	1	22	22	4150
Sep '21	1	1	1	1	14	14	8630
Dec '21	0	0	0	2	13	12	6460

SZVI/Emulsion Application

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**Partitioning
 Into Oil
 Phase**

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**Dissolution &
Degradation**

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Contaminants Depleted

Conclusion

Contact Is Key

- Small droplet size, and mobile emulsions can offer better performance
- Back diffusion and incoming contaminant flux need to be considered

Daughter Products Will Form

- ZVI-assisted bioremediation can minimize daughter concentration and persistence
- Non-stoichiometric quantities of daughters can form

This is a Mass Removal Technique

- Attaining MCL can be challenging in some situations
- Better for grids than permeable reactive barriers

Questions?



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