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AEHS Foundation

REGENESIS®

Materials and methods for the rapid and complete in-situ remediation of source zone contaminants

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Director of Materials Science

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Overview

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

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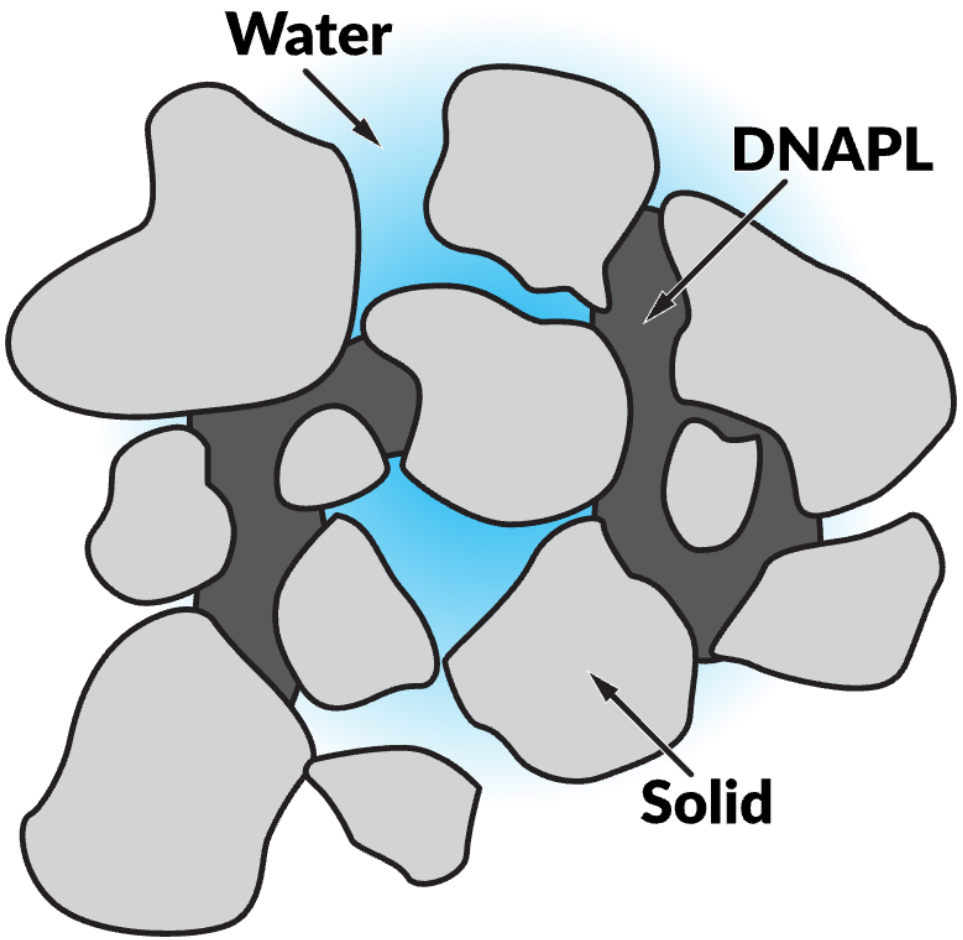
DNAPL Characteristics

- **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**



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Source Zone Remedial Options

Pump and Treat

- Doesn't dislodge adsorbed DNAPL; never ending remedy
- Expensive O&M costs
- Large carbon footprint
- Asymptotic results

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Source Zone Remedial Options

Thermal Treatments

- Usually effective but very expensive

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Source Zone Remedial Options

Thermal Treatments

- Usually effective but very expensive

Excavation

- Effective with depth and infrastructure limitations

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Source Zone Remedial Options

Chemical Oxidation

- Persulfate or permanganate

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Source Zone Remedial Options

Chemical Oxidation

- Persulfate or permanganate

Aerobic Biodegradation

- Calcium peroxide or sparging

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Source Zone Remedial Options

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Source Zone Remedial Options

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Anaerobic Bioremediation

- Sodium lactate/molasses

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Source Zone Remedial Options

Chemical Oxidation

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Aerobic Biodegradation

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Zero Valent Iron/Biogeochemical

Anaerobic Bioremediation

- Sodium lactate/molasses

All operate in the aqueous phase

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Solution: Biological Treatment Using Emulsions and Sulfidated Iron

Co-apply a dilute mixture of:

- Oil-in-water emulsion such as 3DME or EVO
- Sulfidated zero valent iron
- Dechlorinating microbes
- Optionally, nutrients, pH modifiers, B12
- Water

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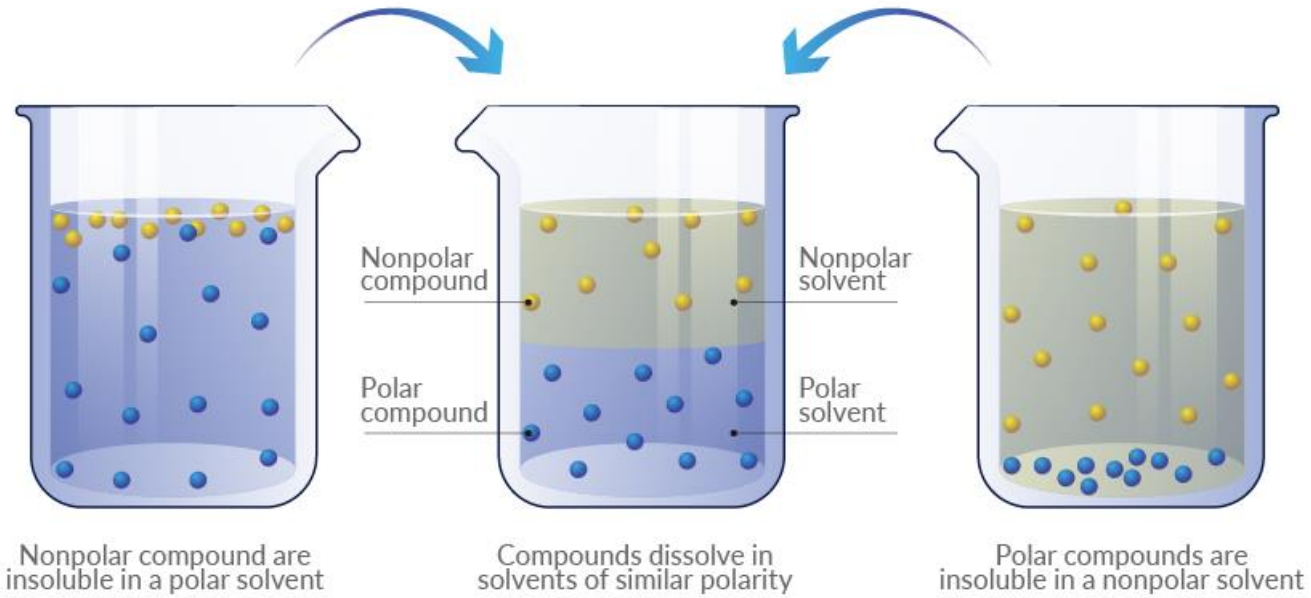
Role of Emulsion

- DNAPL globules/ganglia are hydrophobic
- …and so are droplets of electron 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

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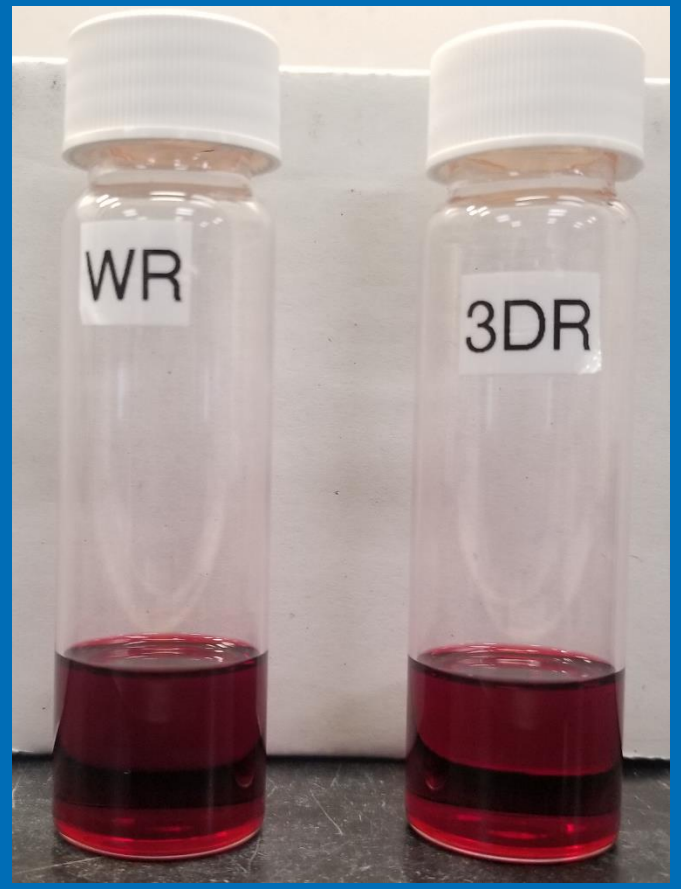
Dye Experiment

Contents:

10 g PCE

4 mg Red Dye



Contents:

10 g PCE

4 mg Red Dye

Dyed PCE

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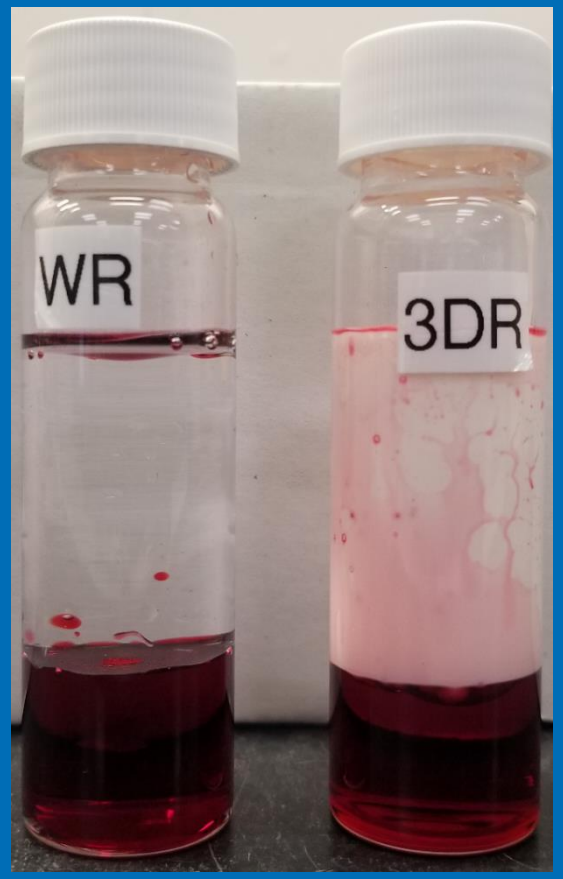
Dye Experiment

Contents:

10 g	PCE
4 mg	Red Dye
30 mL	Water



Before Shaking

Contents:

10 g	PCE
4 mg	Red Dye
30 g	3DME

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Dye Experiment

Contents:

10 g	PCE
4 mg	Red Dye
30 mL	Water

Shake and Wait 1 Hour

Contents:

10 g	PCE
4 mg	Red Dye
30 g	3DME

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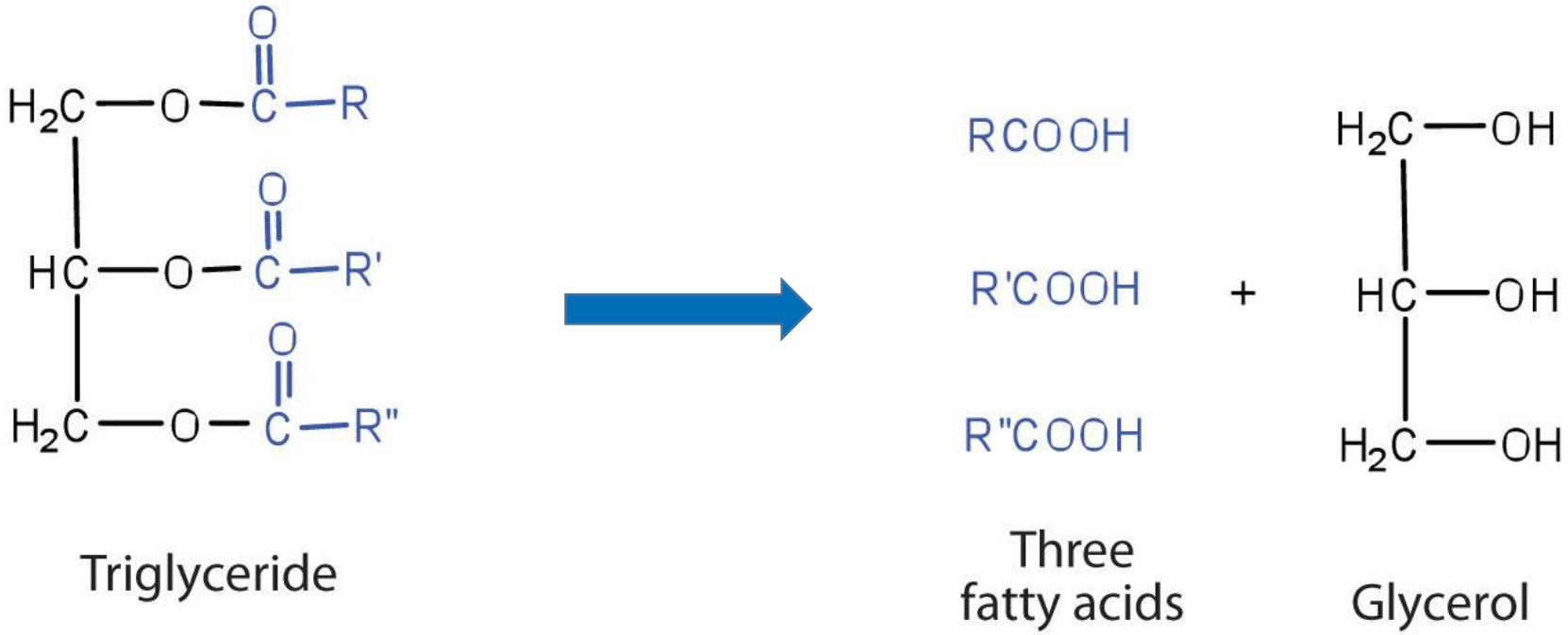
Oil Droplet Degradation and Contaminant Release

Vegetable Oil Droplets are Biodegraded

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



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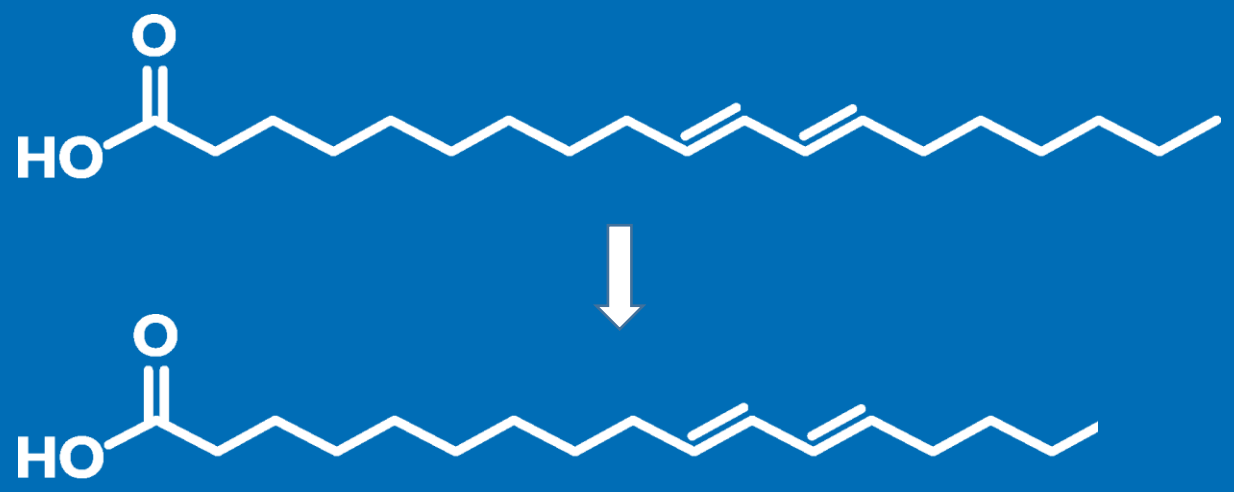
Oil Droplet Degradation and Contaminant Solubilization

Volatile Fatty Acids are Biodegraded



Lineolic acid

$$C_{18}H_{32}O_2 + 2\ H_2O$$

$$\downarrow$$

$$C_{16}H_{28}O_2\ +\ 2\ H_2\ +\ C_2H_4O_2$$

VFA (C_{16}) + molecular hydrogen + acetic acid

Partitioning DNAPL Into The Aqueous Phase

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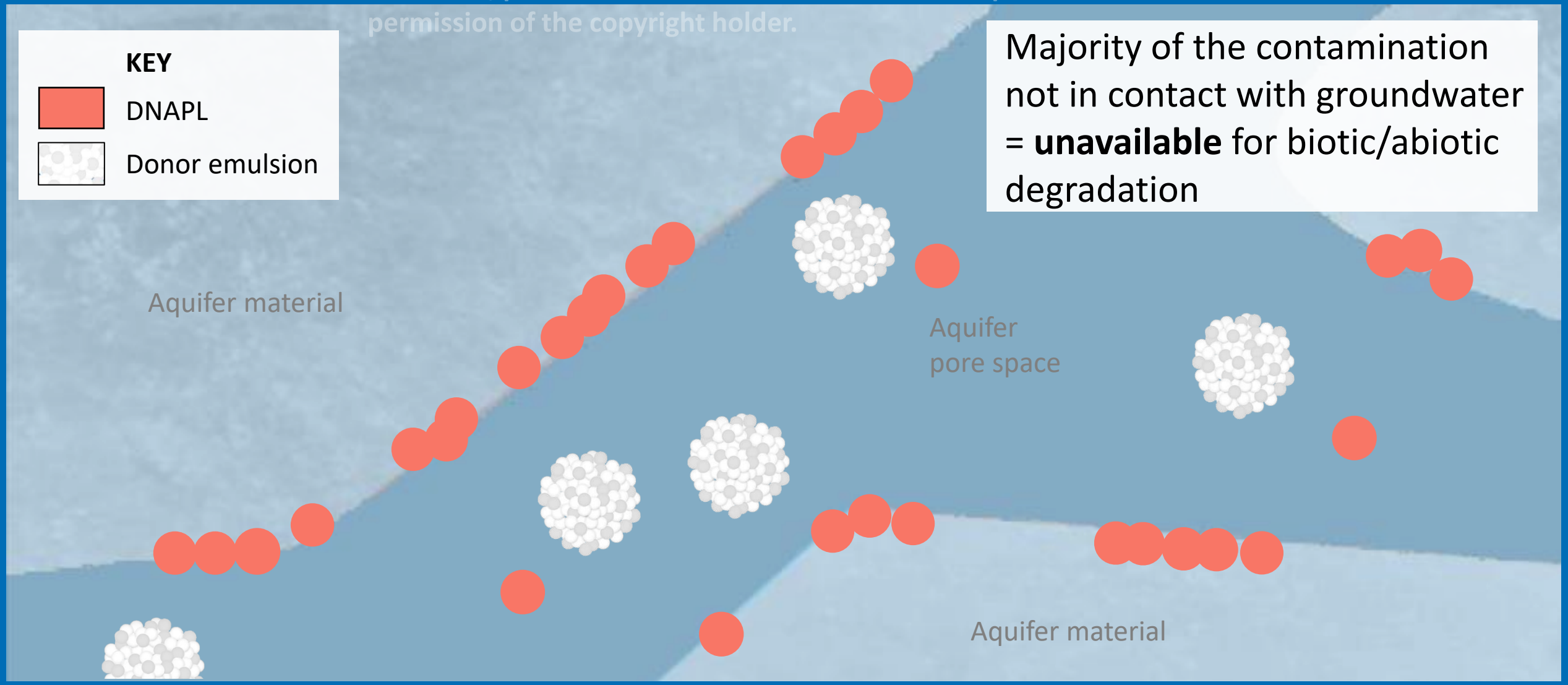

Partitioning DNAPL Into The Aqueous Phase

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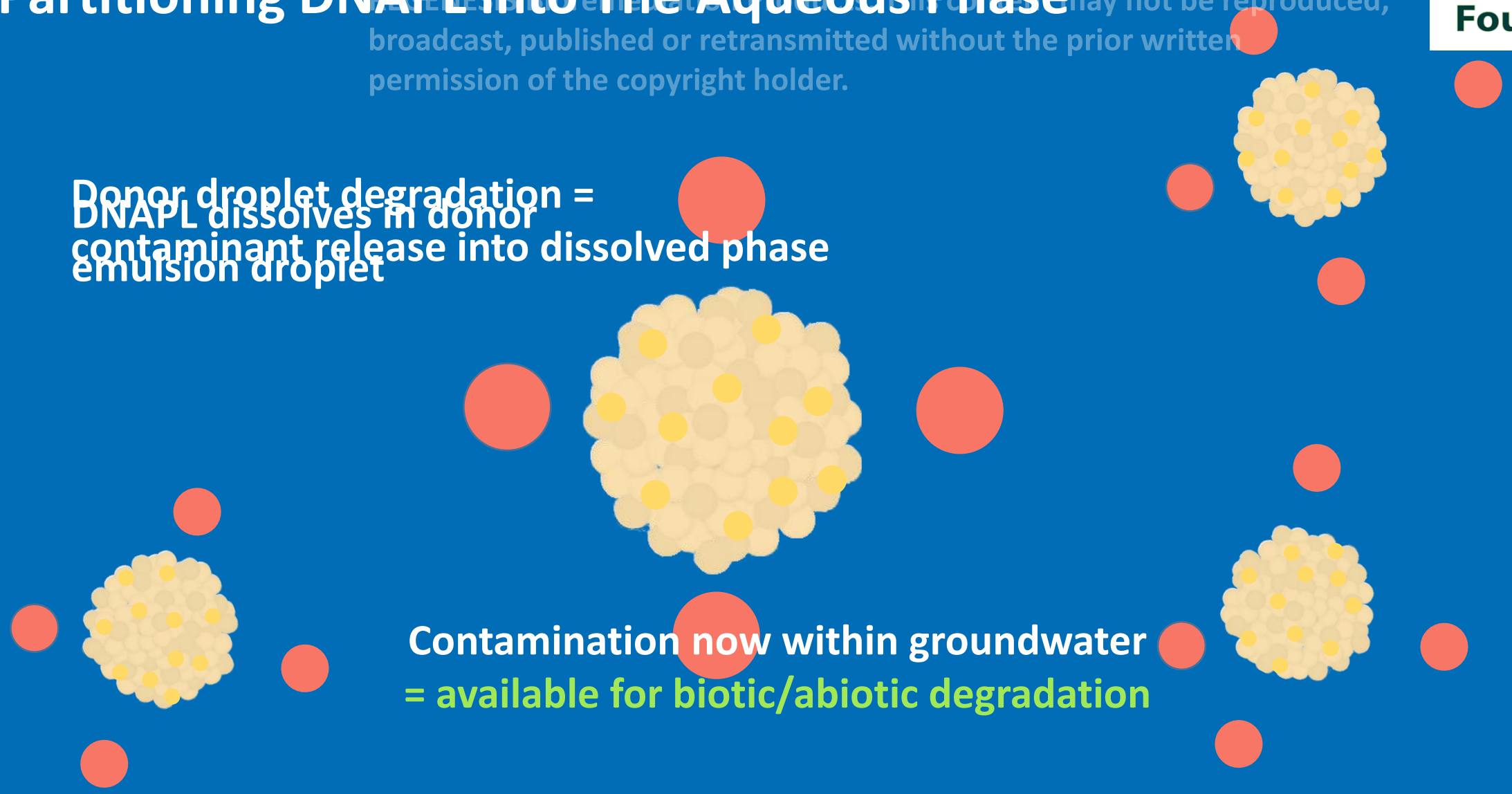
Donor droplet degradation = contaminant release into dissolved phase

DNAPL dissolves in donor emulsion droplet



Contamination now within groundwater

= available for biotic/abiotic degradation

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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

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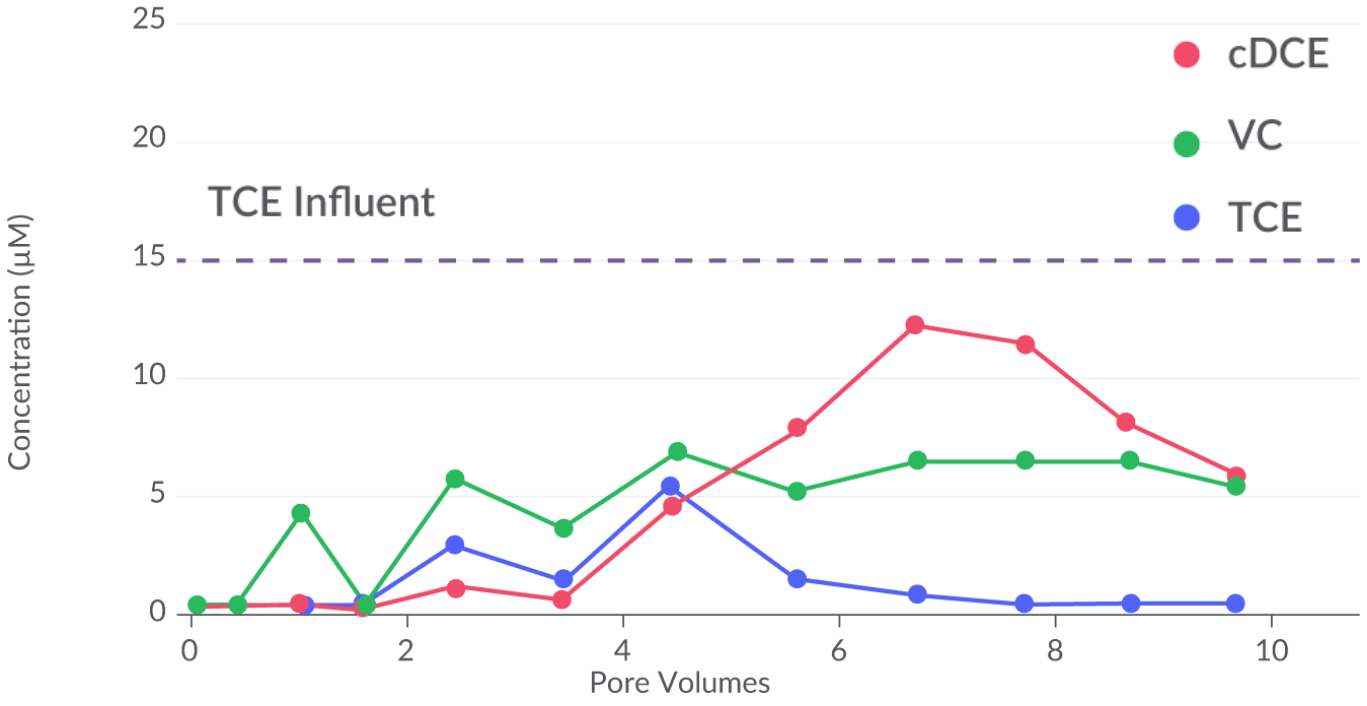
Biological Approach: Column Study

- 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



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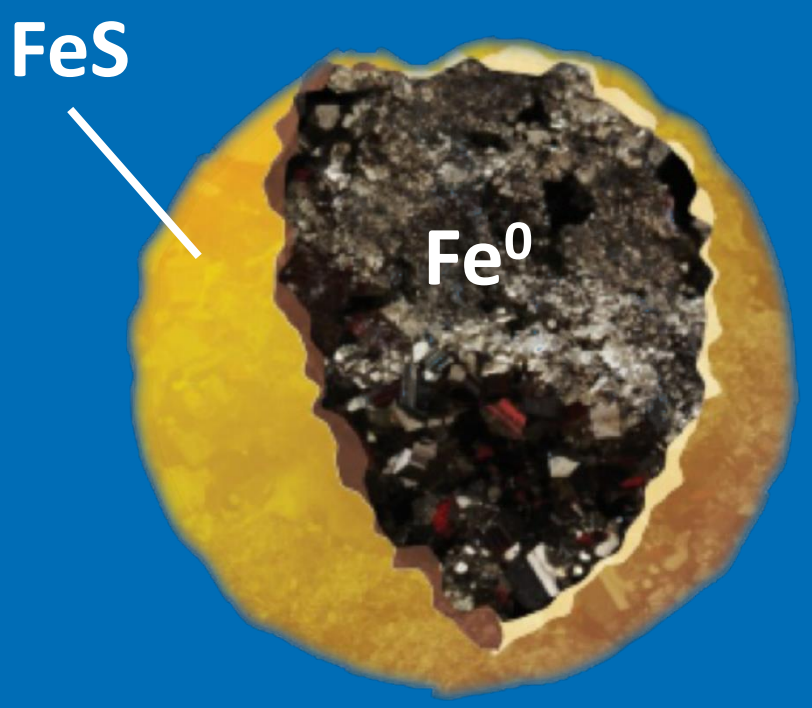
SZVI Accelerated Biodegradation

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



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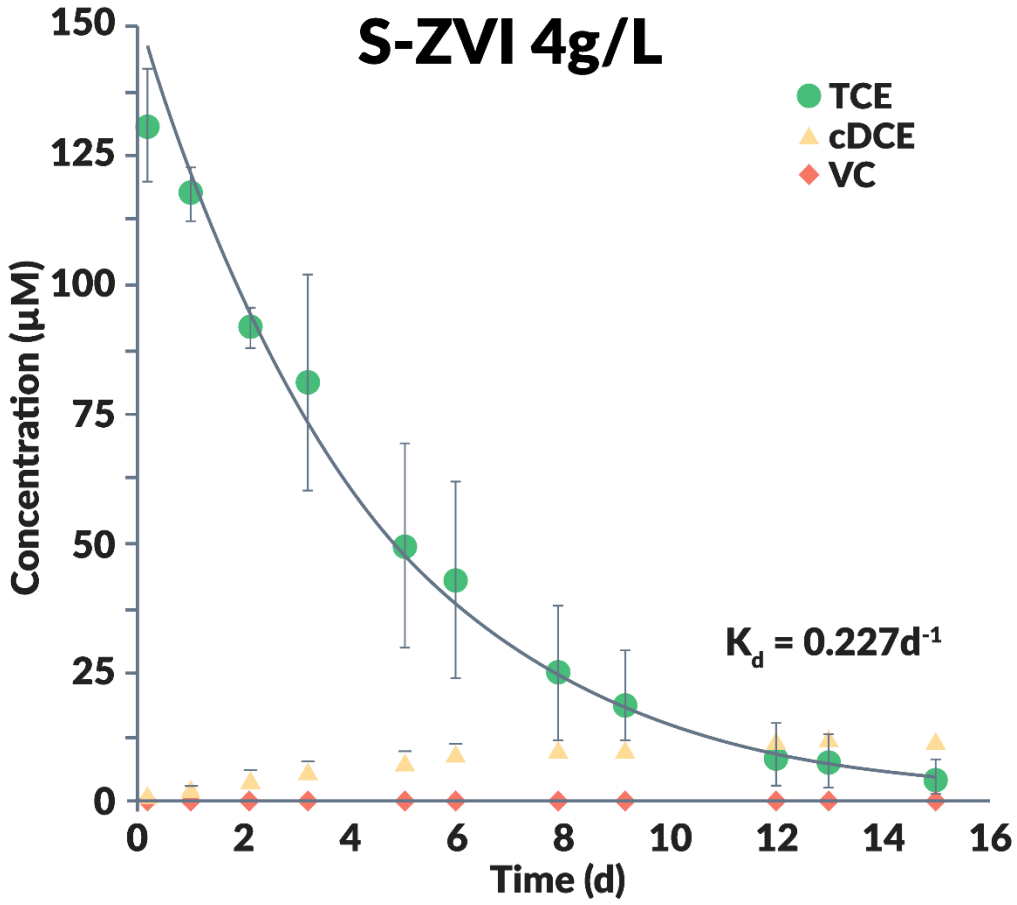
S-MicroZVI Reactivity: TCE



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

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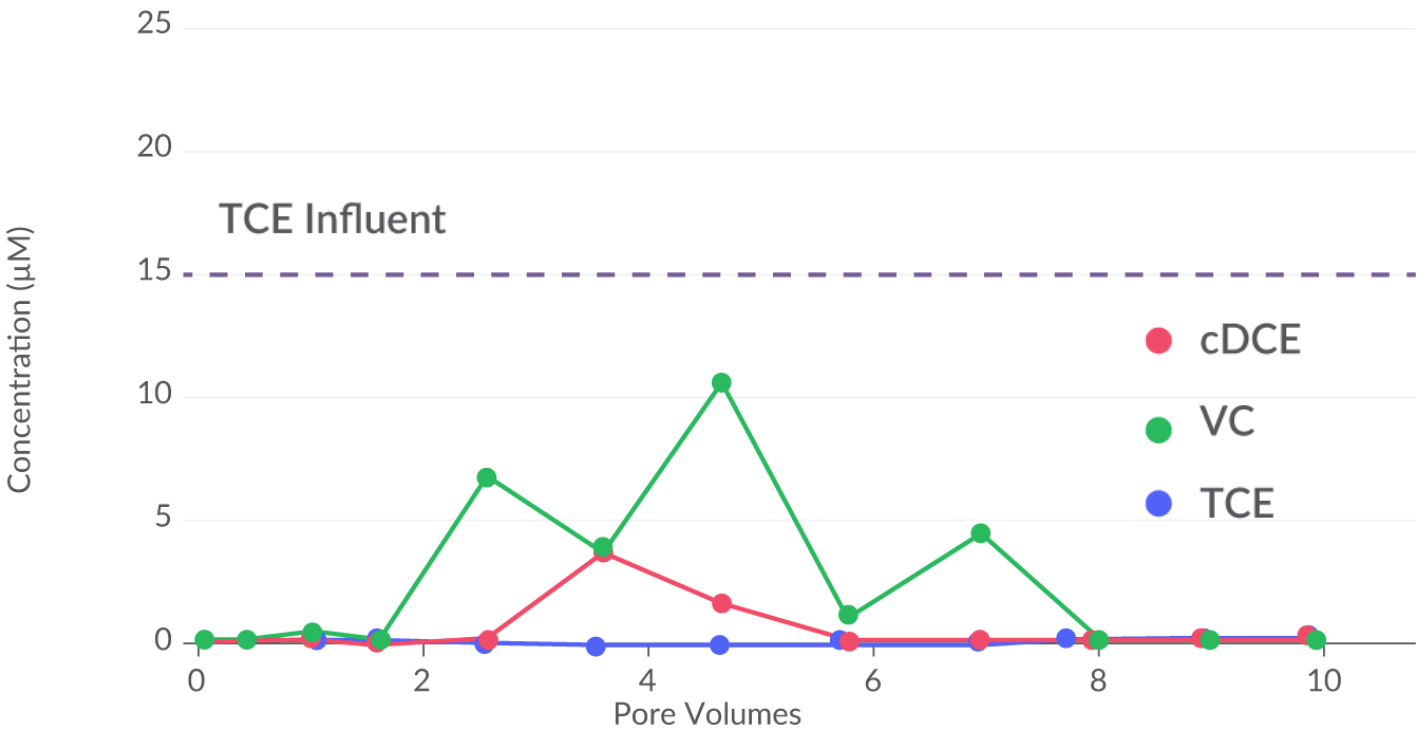
Combining Biological and Abiotic: Column Study

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



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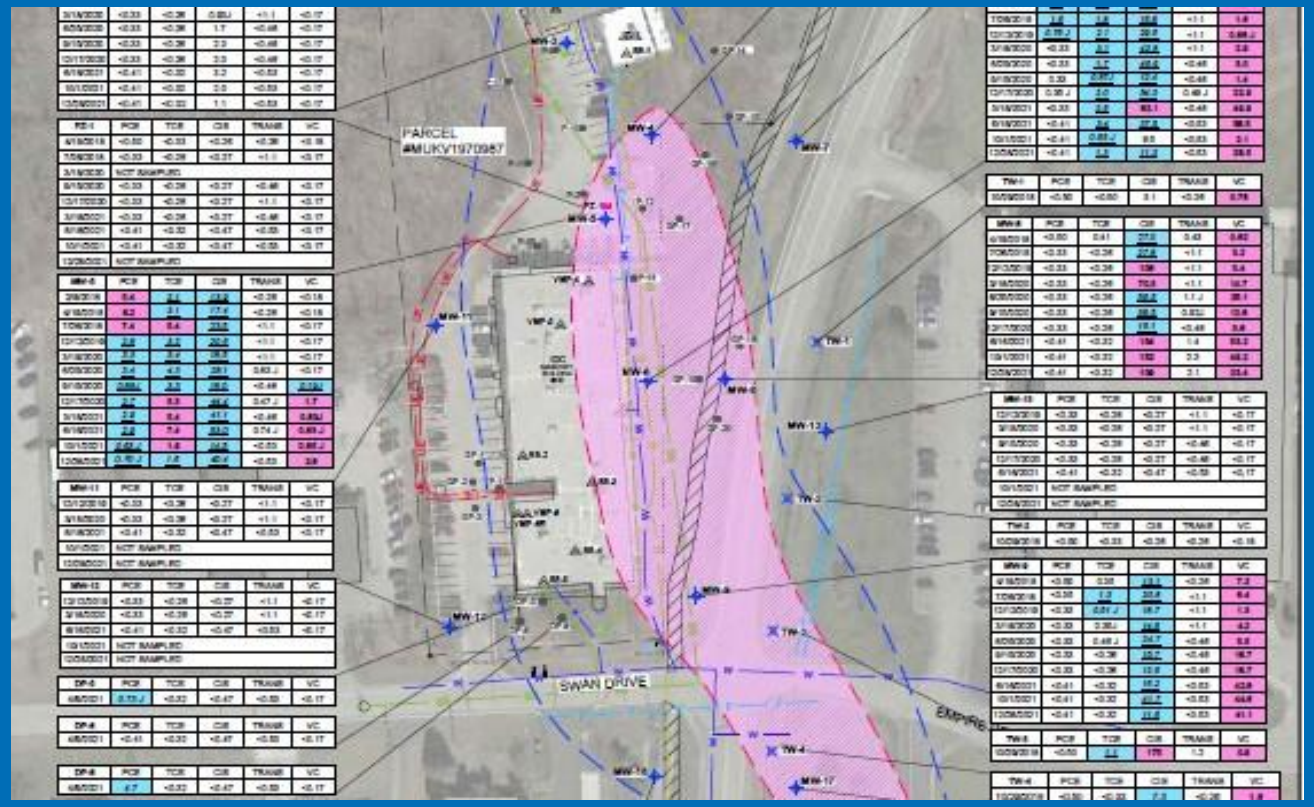
SZVI Emulsion Application

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



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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

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SZVI/Emulsion Application

Monitoring Results: CVOC and Dissolved Gases

Partitioning Into Oil Phase

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Dec ’19	132	19	33	3	26	25	43
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Dissolution & Degradation

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Contaminants Depleted

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Comparison with EZVI

	SZVI/Emulsion	Emulsified Vegetable Oil
Organic	~ 2 micrometer vegetable oil	Continuous phase veg oil
ZVI	2-3 micrometer SZVI	> 10 micrometer ZVI
Viscosity	Waterlike	> 500 cP
Injection pressures	Typically < 50 psi	Typically > 200 psi
Distribution	Intragranular	Channeling/Fractures

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Caveats and Practical Limitations

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

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Questions?

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