Optimization and Advances in Amendments for Chlorinated Solvent Sites

AEHS Foundation

32nd Annual International Conference on Soil, Water, Energy, and Air

Tuesday, March 21 , 2023
2:30 PM – 3:00 PM

tersus environmental

Agenda

Bioremediation
Biological Reductive Dechlorination

01

02

Emulsified Vegetable Oils
History and Advancements

In Situ Alcoholysis
Transesterification of Vegetable Oils

03

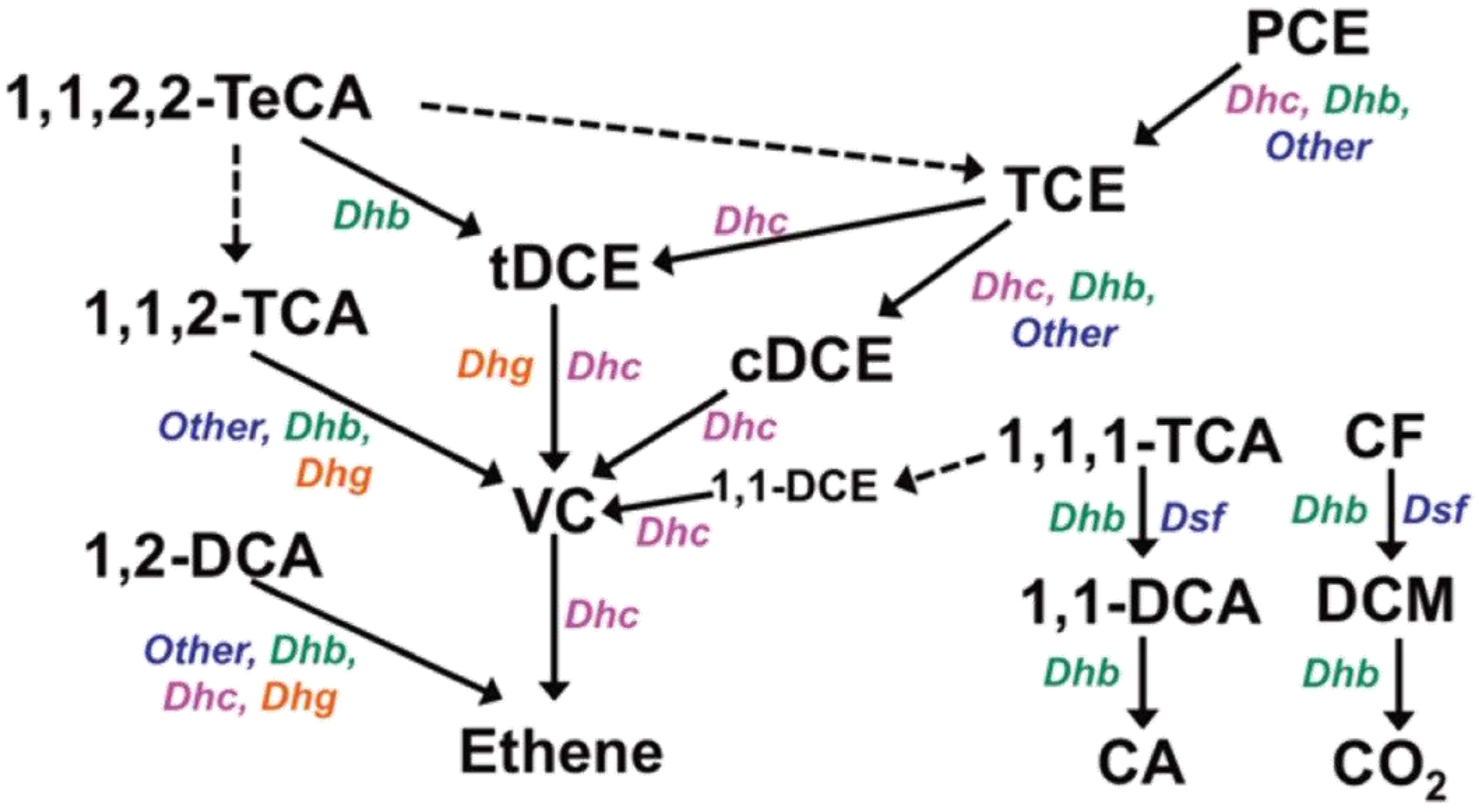
04

Heat Enhanced Reductive Bioremediation
Benefits of this approach

What is needed for enhanced reductive dechlorination?

Vegetable oils ferment to acetic acid and hydrogen

Overview chlorinated solvent dechlorination pathways and organisms responsible



Dhc = Dehalococcoides
Dhg = Dehalogenimonas
Dhb = Dehalobacter
Other = e.g., Desulfitobacterium (Dsf), Sulfurospirillum, Geobacter
----- Dashed lines are abiotic reactions

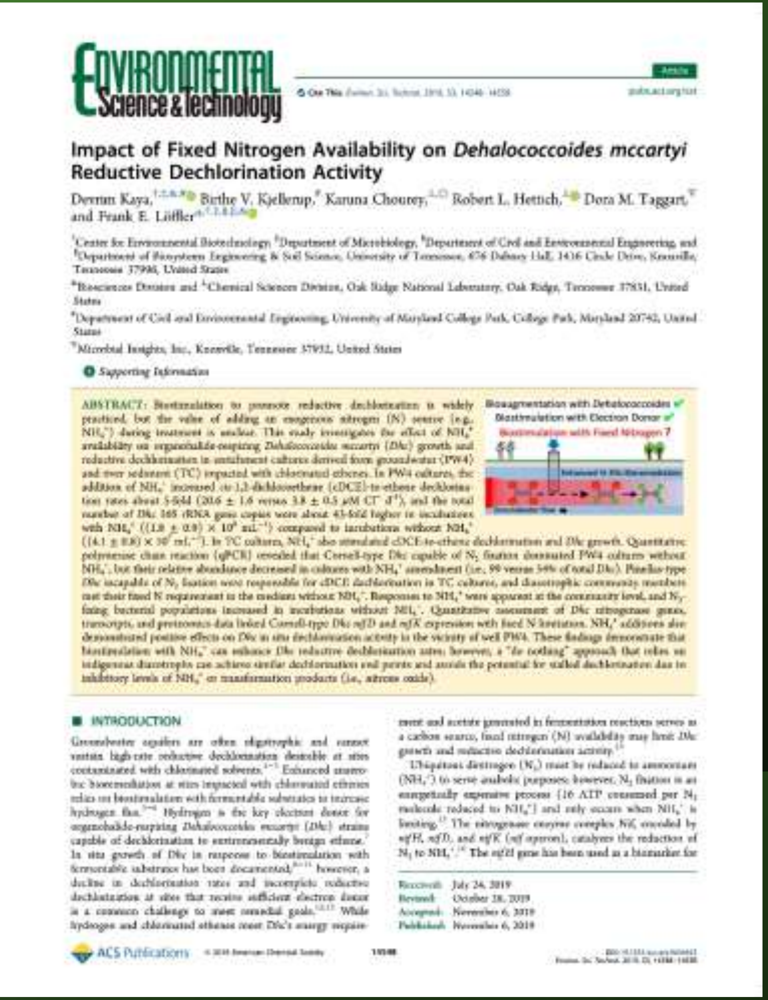
Wei K., Grostern A., Chan W.W.M., Richardson R.E., Edwards E.A. (2016) Electron Acceptor Interactions Between Organohalide-Respiring Bacteria: Cross-Feeding, Competition, and Inhibition. In: Adrian L., Löffler F. (eds) Organohalide-Respiring Bacteria. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-662-49875-0_13

EDS-ER™

Electron Donor Solution – Extended Release

Water soluble vegetable oil

USDA CERTIFIED BIOBASED PRODUCT
PRODUCT 99%
FP


Environmental Science & Technology

Impact of Fixed Nitrogen Availability on *Dehalococcoides mccartyi* Reductive Dechlorination Activity

Deniz Kaya, Birthe V. Kjellerup, Karuna Chourey, Robert L. Hettich, Dora M. Taggart, and Frank E. Löffler

INTRODUCTION

Environ. Sci. Technol. 2019, 53, 24, 14548–14558

Nutrients

- Biostimulation benefits from adding an exogenous nitrogen (N) source (e.g., NH_4^+)
- Addition of NH_4^+ increased cis-1,2-dichloroethene (cDCE)-to-ethene dichlorination rates about 5-fold
- Typical target dosing:
  - 20:1 BOD to NH_3 – N ratio
  - 100:1 BOD to PO_4 – P ratio

TersOx™ Nutrients-QR

- Fast-acting soluble nutrient blend for bioremediation
- Blend of nitrogen, phosphorous and microbial growth enhancers that provide a source of urea, phosphate and potassium

Vitamin B_{12}

- *Dehalococcoides mccartyi strains* require vitamin B_{12} (Yan et al, 2013)
- Reported concentration for optimal dechlorination and growth: 25 to 50 µg/L (Stroo et al., 2013)

Stroo et al., 2013, Bioaugmentation for Groundwater Remediation, edited by Stroo, H.F., Leeson, A., Ward, C.H. HydroGeoLogic, Inc., Ashland, OR, USA

Yan et al, 2013, Yan J, Im J, Yang Y, Löffler FE. 2013 Guided cobalamin biosynthesis supports *Dehalococcoides mccartyi* reductive dechlorination activity. Phil Trans R Soc B 368: 20120320. http://dx.doi.org/10.1098/rstb.2012.0320

Distribution of the Correct Type of Fatty Acids is Essential

Acetate

- Slow consumption
- Will migrate downgradient
- Stimulates PCE -> TCE -> cDCE
- Will not stimulate cDCE -> VC -> ethene

Hydrogen (H_2)

Produced from linolenic acid, propionate, butyrate, etc.

- Rapid consumption
- Does not migrate beyond injection zone
- Required for cDCE -> VC -> ethene

(12) **United States Patent**
Birk et al.

(10) **Patent No.: US 11,577,231 B2**
(45) **Date of Patent: Feb. 14, 2023**

(54) ENHANCED REDUCTIVE BIOREMEDIATION METHOD USING IN-SITU ALCOHOLYSIS

(71) Applicant: **Tersus Environmental LLC**, Wake Forest, NC (US)

(72) Inventors: **Gary M. Birk**, Wake Forest, NC (US); **David F. Alden**, Scranton, PA (US)

(73) Assignee: **Tersus Environmental LLC**

(21) Appl. No.: **16/797,617**

(65) **Prior Publication Data**

(51) **Int. Cl.**

(52) **U.S. Cl.**

(58) **Field of Classification Search**
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

FOREIGN PATENT DOCUMENTS

OTHER PUBLICATIONS

* cited by examiner

(57) **ABSTRACT**

20 Claims, 5 Drawing Sheets

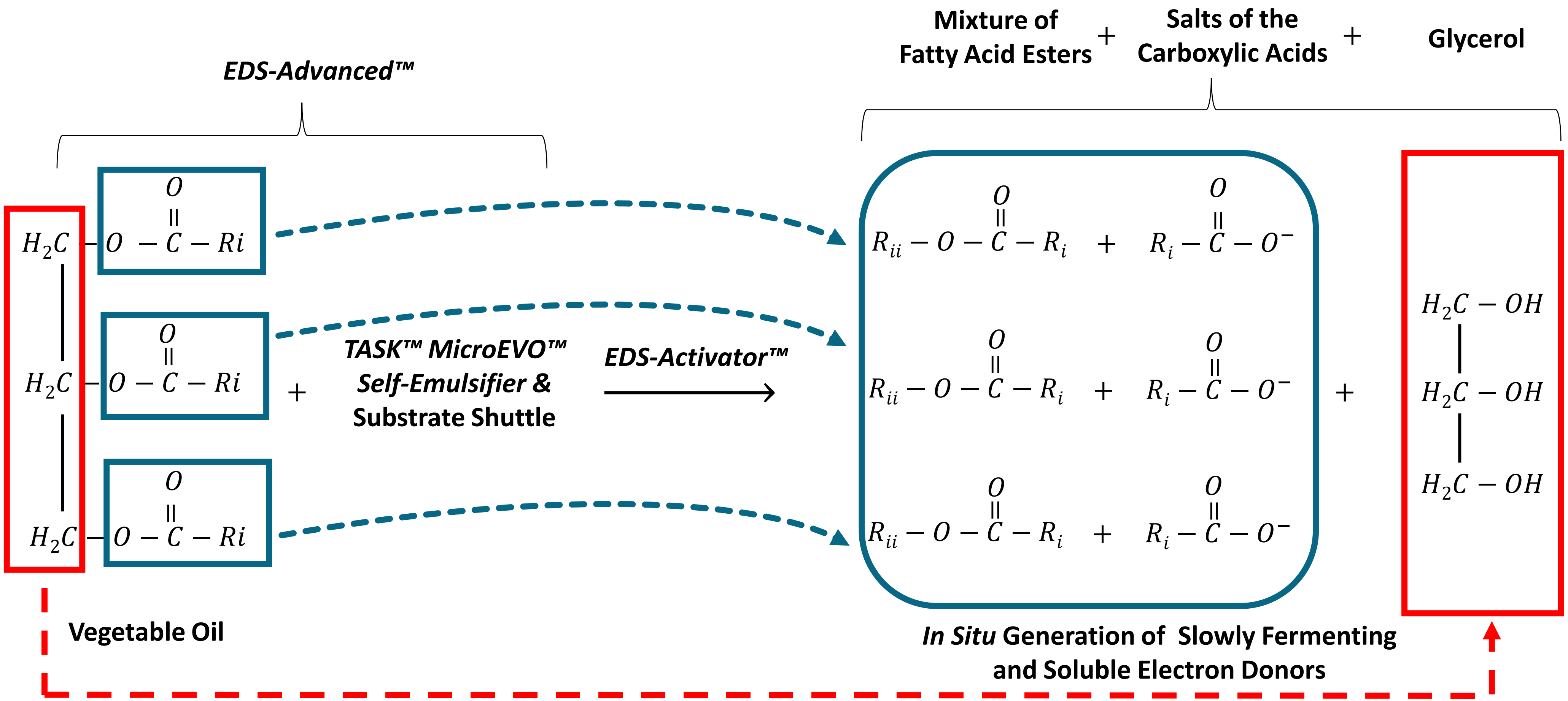
Deploying Electron Donor via *In Situ* Alcoholysis

Definitions

- **Alcoholysis:** A reaction in which an alcohol is a reactant and becomes part of the reaction product.

- **Transesterification:** The chemical conversion process of triglycerides with alcohol into fatty acid esters with the help of a catalyst.

In Situ Transesterification of Vegetable Oils



Activator Options

Hydroxide base-catalyzed transesterification of triglycerides

- Homogeneous Alkaline Catalyst
  - Alkyl oxides (RO^-)

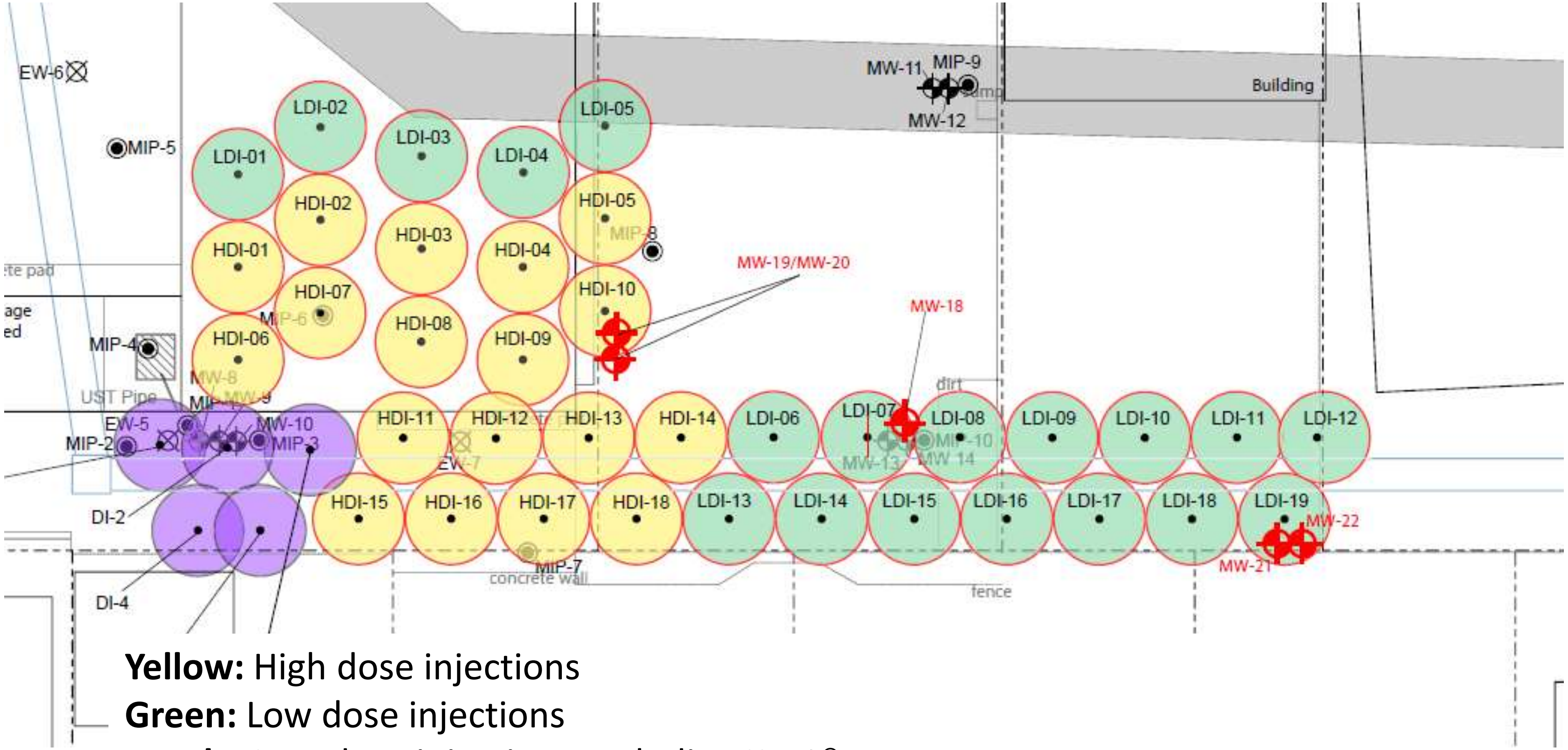
Lipase-catalyzed hydrolysis of triglyceride

- Biocatalyst
  - Enzyme (triglyceride lipases)

Typical Application Rates

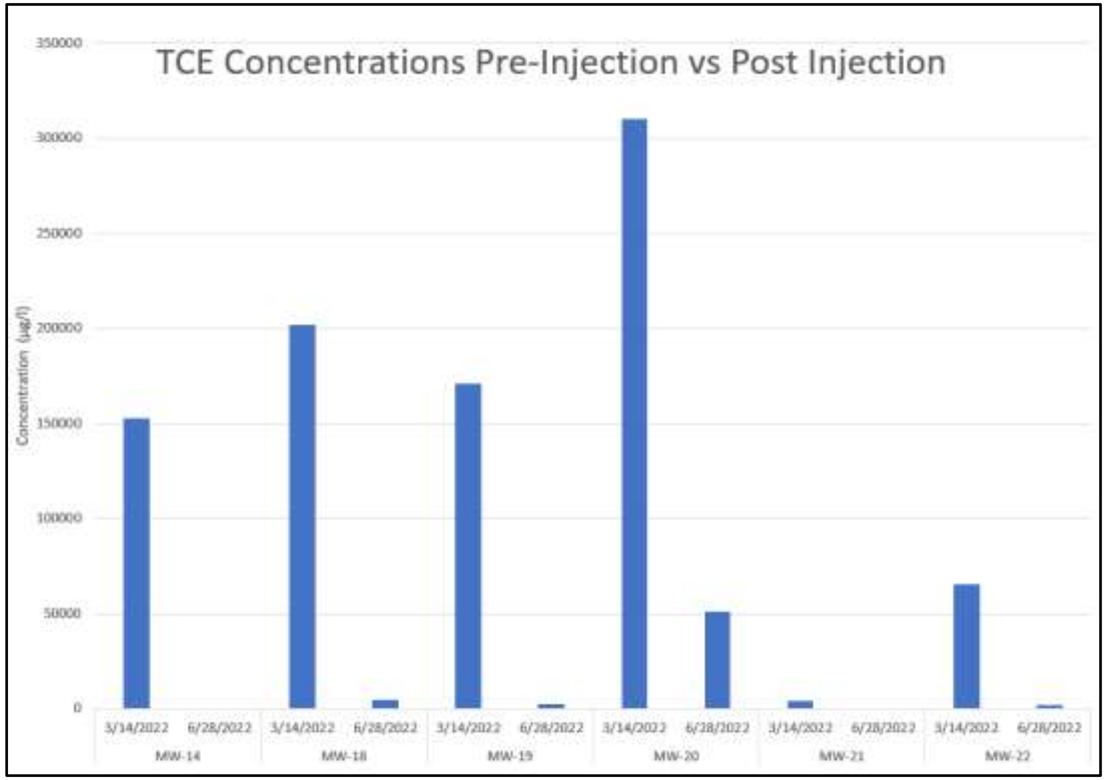
EDS-ER™ (Soybean Oil and TASK™ MicroEVO™ Self-Emulsifier	2 to 8 g/L
EDS-Activator™	16 to 20% of EDS-ER™ Dose
EDS Substrate Shuttle (Co-Solvent)	0.4 g/L
Microscale Zero-Valent Iron (mZVI)	4 to 6 g/L

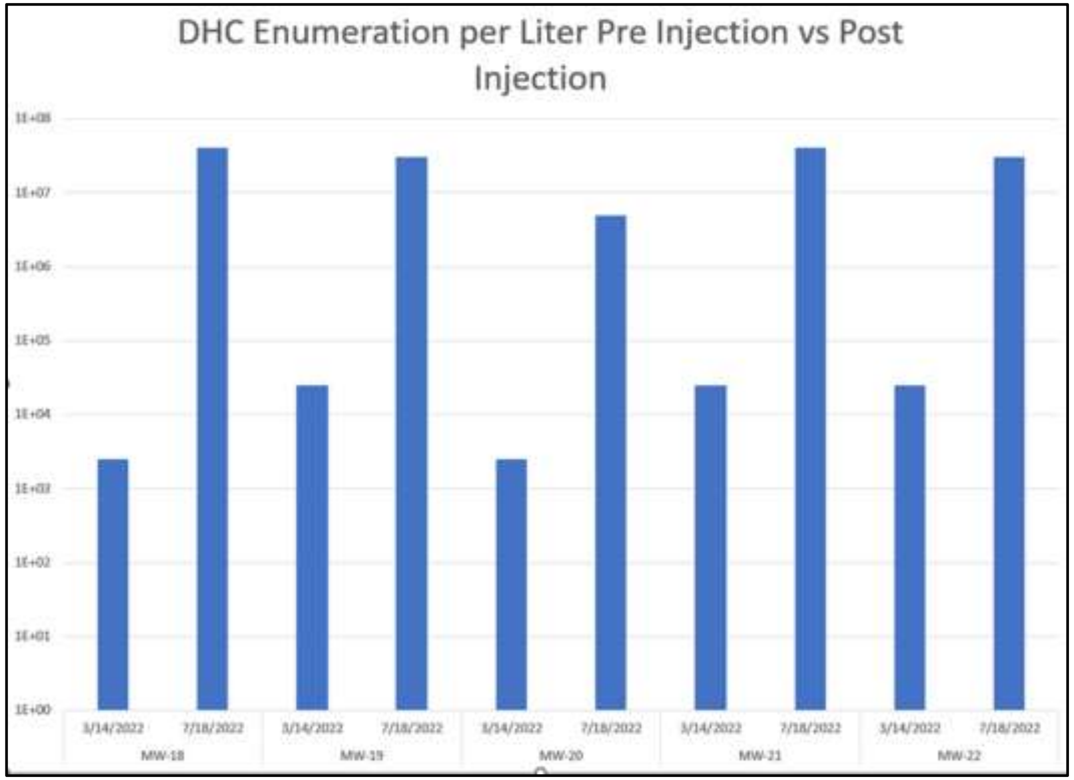
TCE Site



Yellow: High dose injections
Green: Low dose injections
Purple: Low dose injections excluding KB-1®

Injection Results





EDS-Advanced™

Unrestricted Electron Donor Subsurface Distribution for Anaerobic Bioremediation

- Improved subsurface distribution of a vegetable oil-based electron donor
- Improved ROI, fatty acid distribution and TOC when compared to EVO
- Eliminates dependence on EVO droplet size
- Aids in reducing cVOC inhibitory concentrations by sequestering DNAPL
- High alcohol content and high solubility reduces injection well biofouling risk

Enhancement Options

Apply Heat

- Enhances transesterification reaction
- Reduces time from days to months to minutes to hours
- 6 minutes
  - ✓ 90°C – 94% yield
  - ✓ 32°C – 64% yield

Optimum Growth Temperature

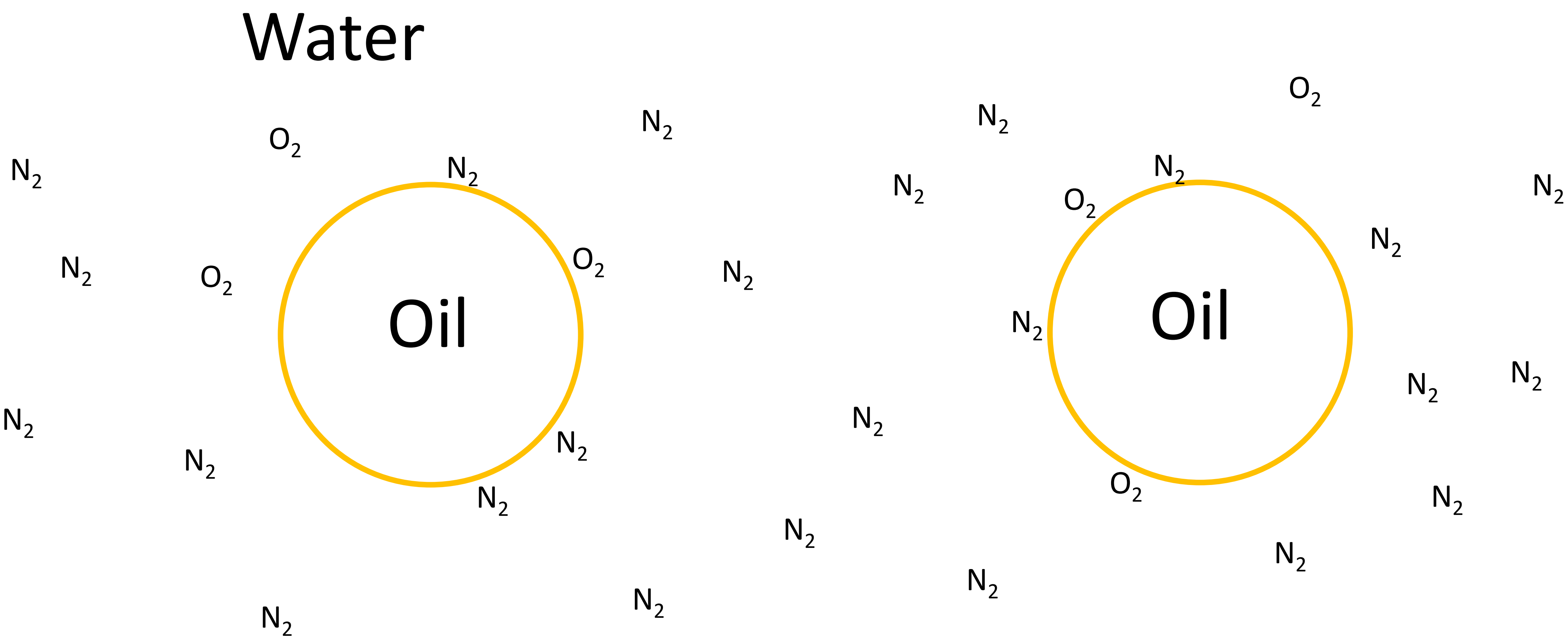
- 25-30°C hydrogenotrophic Dhc strains (Löffler et al., 2013)
- <40−45°C biotic or abiotic destruction
- > 50°C very little biotic or abiotic destruction (Stroo et al., 2013; Costanza et al., 2009)

Hot water vs cold water

- Hot water dissolves fewer gases (e.g., oxygen or carbon dioxide)

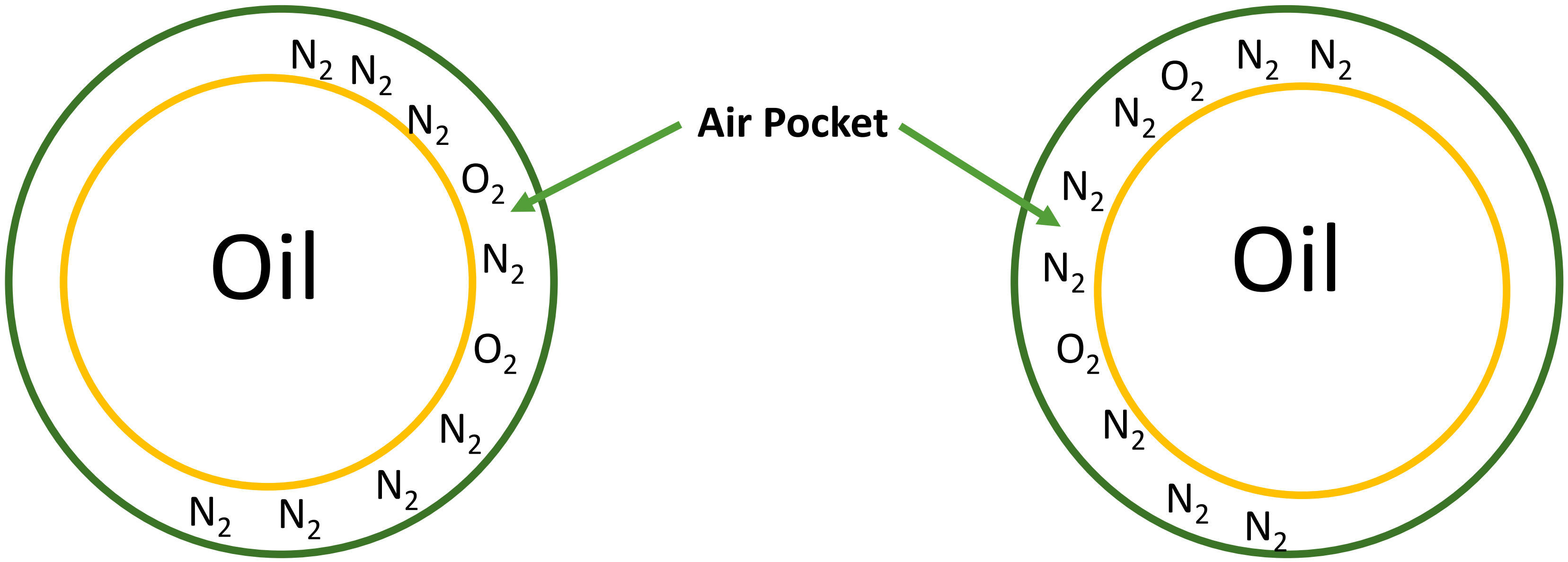
- Hot water dissolves more solids (e.g., sugars)

Example of dissolved gas in water with oil

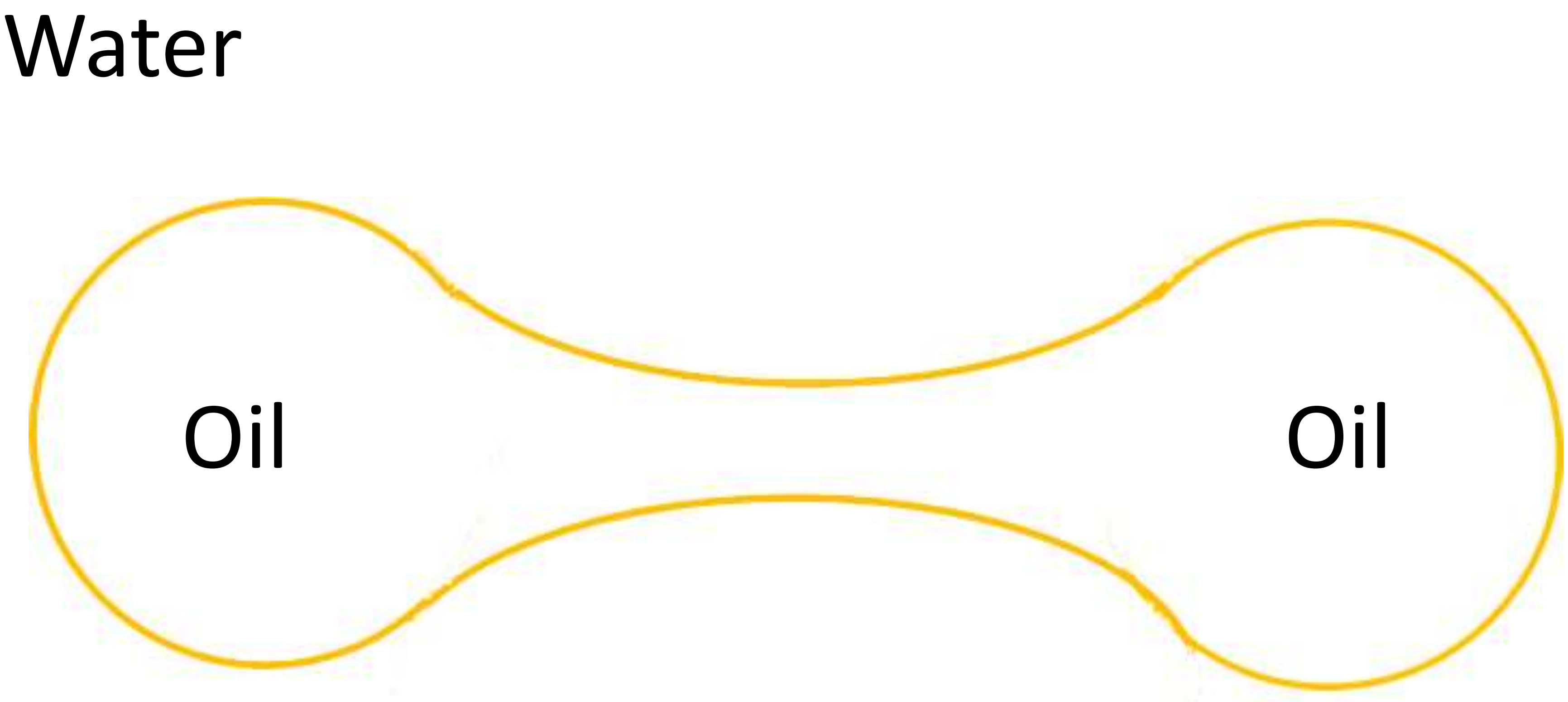


The dissolved gas adsorbs to the surface of the oil

Water

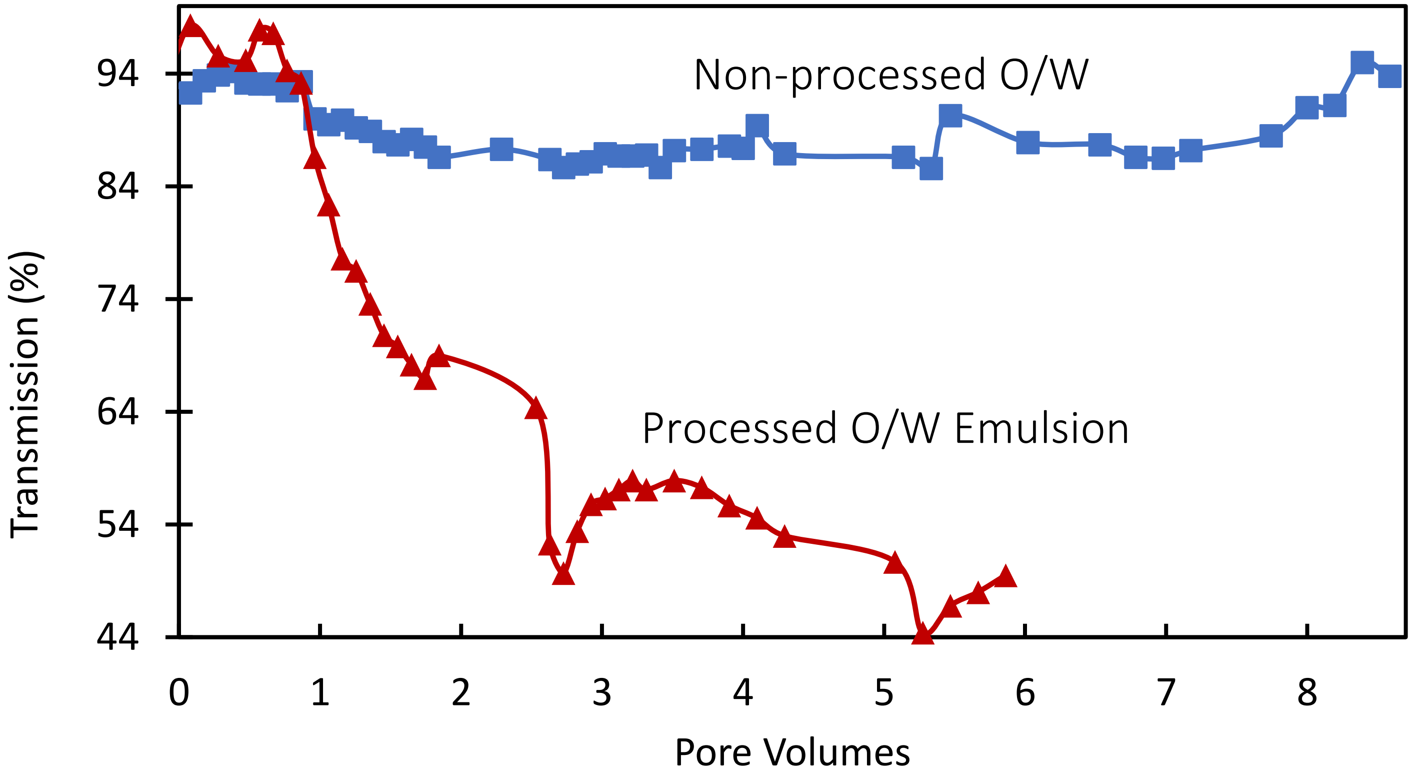


Surface tension pushes oil droplets together to form one big droplet



Processed Emulsions Remain Stable in Flow Through Porous Media

Photo of processed O/W emulsion after 1 hour



Heating Options

Conventional

- Residual heat from an *in situ* thermal remediation project
- Electrical resistance heating
- Thermal conduction heating

Heat amendments / water and inject

- Hot water boiler
- Shell and tube heating tank or a batch heating tank with coils
- Solar collector, thermal storage tank with a submerged heat exchanger and an auxiliary heat exchanger

Hot Water Injection

Hydrogeological parameters

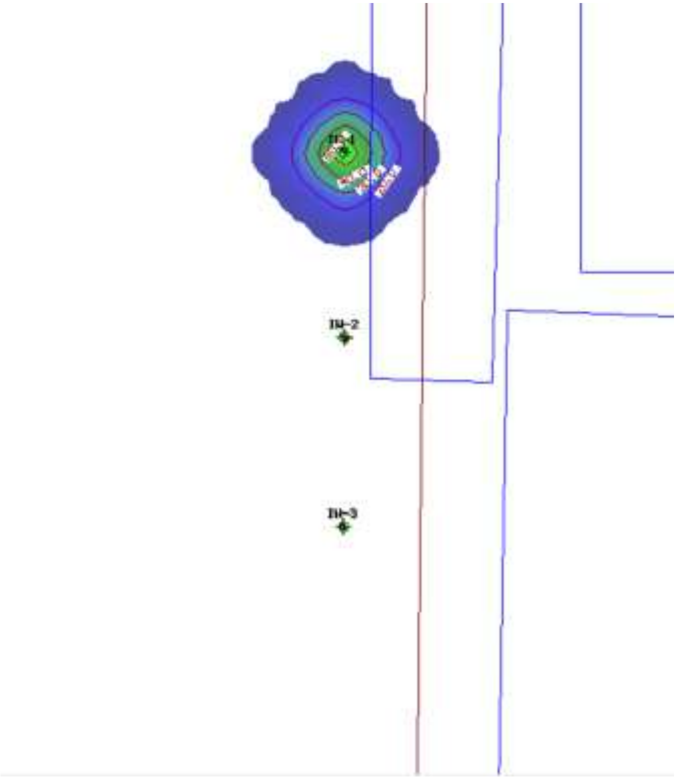
- Site lithology: sand
- Porosity: 0.33
- Aquifer hydraulic conductivity K of 1x10-2 cm/s
- Hydraulic gradient: 0.002 feet/feet

Injection

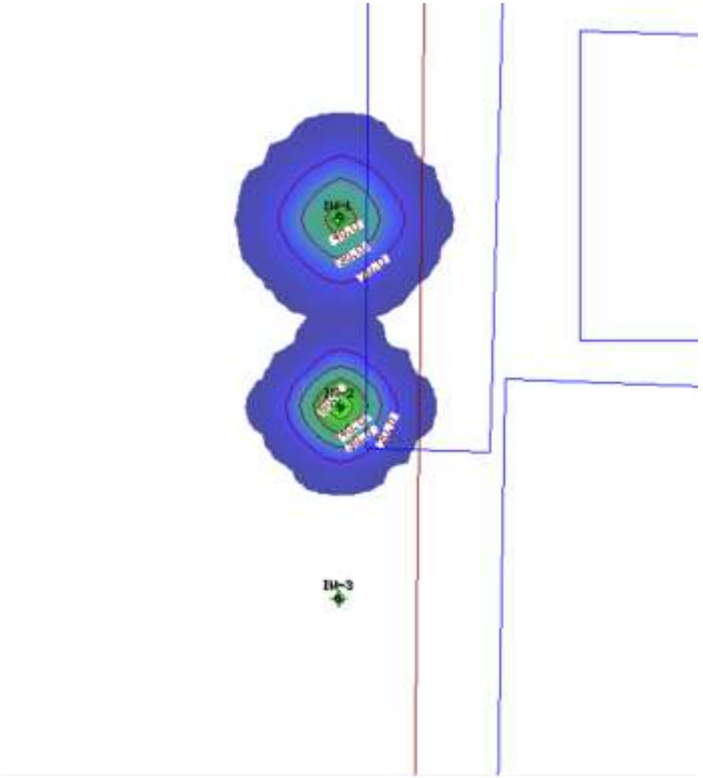
- 12-hour injection event
- 75 m^3 (19,813 gallons) of water heated to 90°C
- 150 m^3/d (27.5 gpm) flow rate

Model Results

Time = 0.5 days

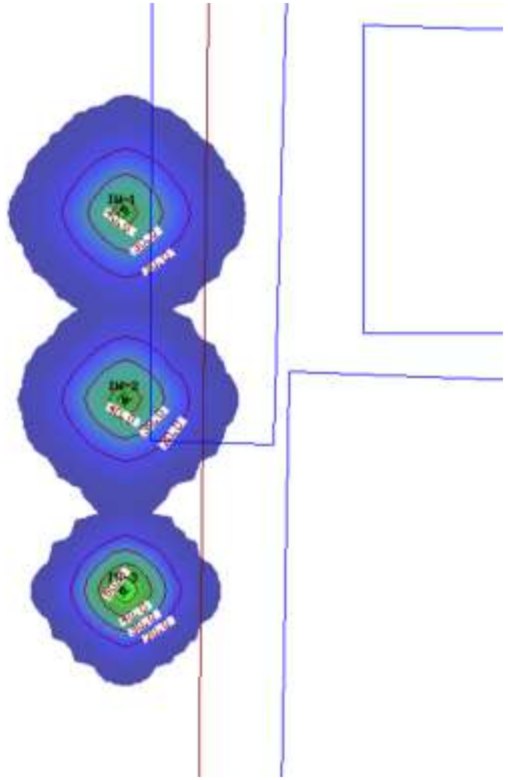


Time = 1 day

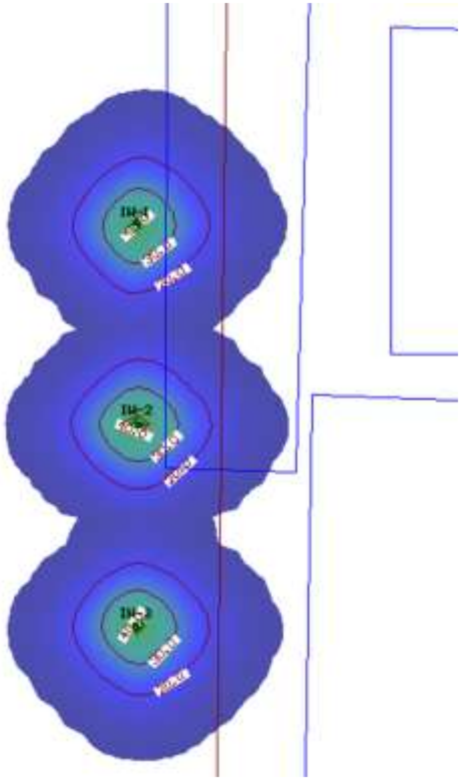


Model Results (continued)

Time = 1.5 days

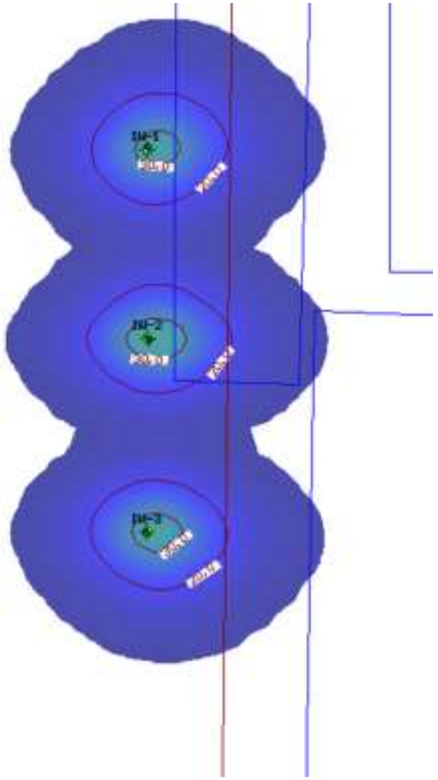


Time = 5 days

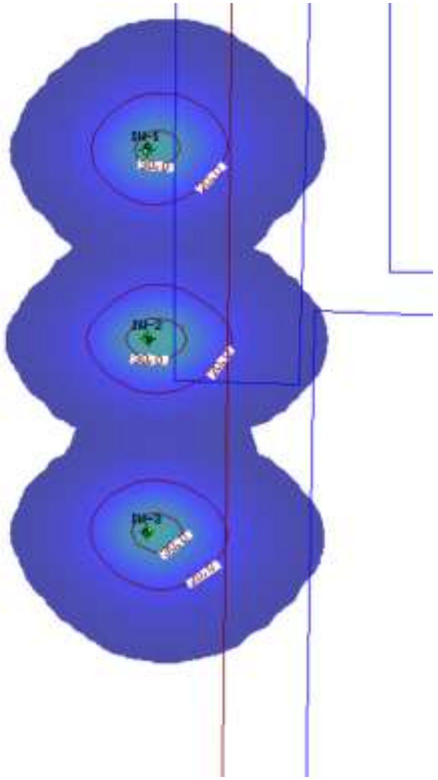


Model Results (continued)

Time = 10 days

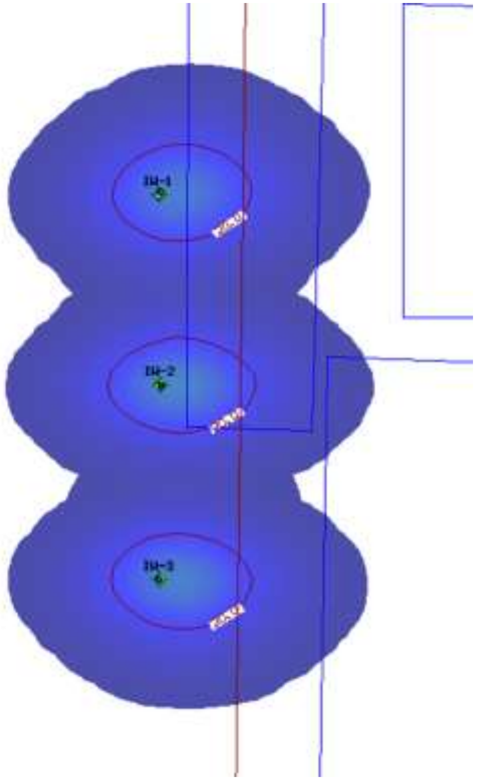


Time = 30 days

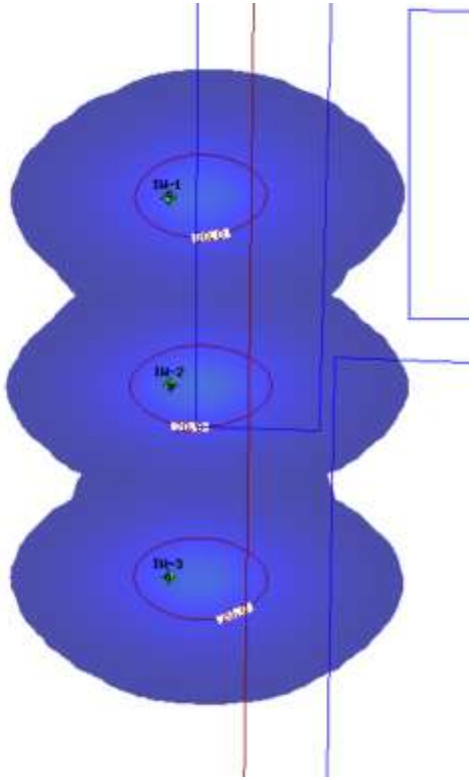


Model Results (continued)

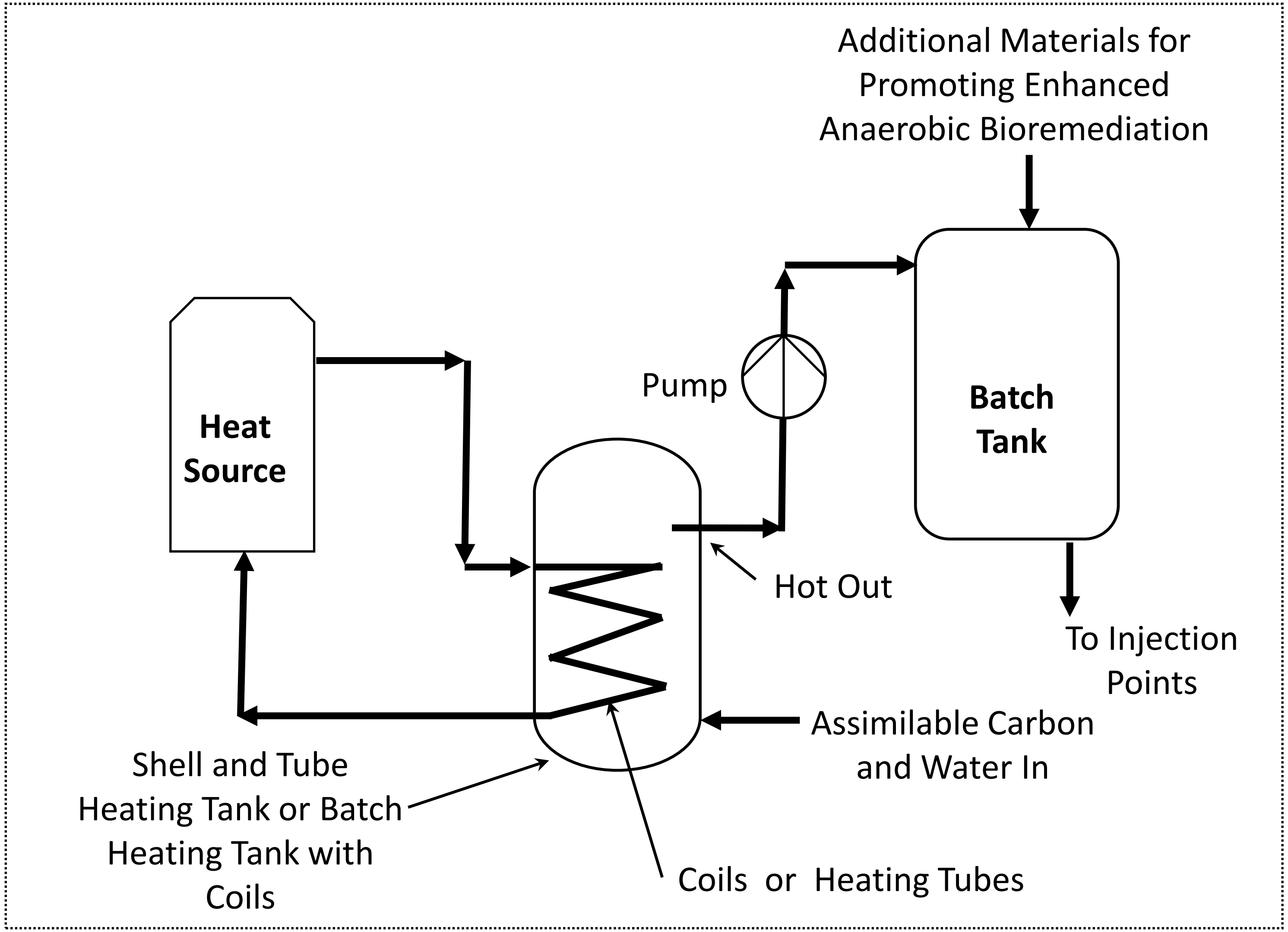
Time = 60 days



Time = 90 days



Shell and Tube Heating Tank or Batch Heating Tank with Coils



Heat Enhanced Reductive Bioremediation

- Microbes that do all the work like a warm environment
- Warm water has lower dissolved gases
- Heating increases the alcoholysis reaction rates

Thank you

Gary M. Birk, P.E. (NC, VA, & FL)
Tersus Environmental
T. + 1 919 453 5577 x2001 | M. + 1 919 638 7892
gary.birk@tersusenv.com | tersusenv.com

tersus environmental