Heat-Enhanced Catalyzed Reductive Bioremediation

Wed., November 15, 2023

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Agenda

01 Overview

Optimal Dechlorination Conditions
& Average Groundwater Temperatures

02 Catalyzed Enhanced Reductive Bioremediation

03 Heat Catalyzed Enhanced Reductive Bioremediation

04 Heating Options

Benefits of this approach

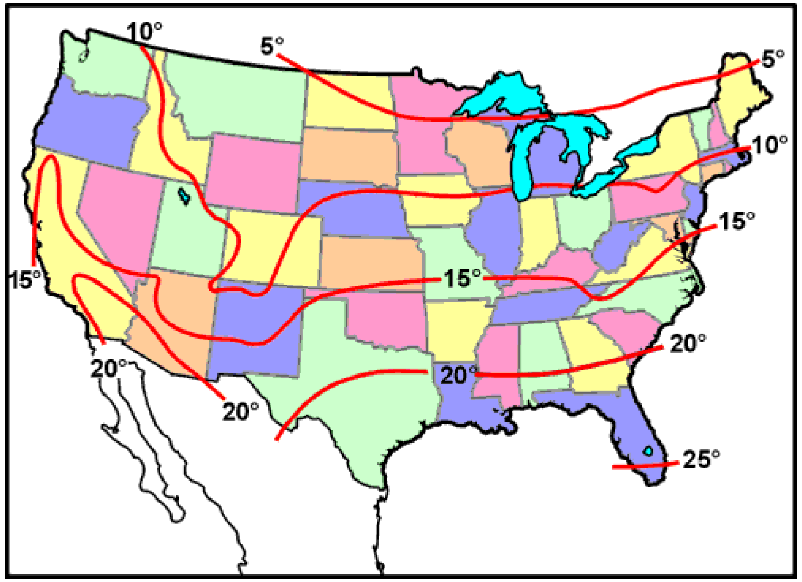
What is needed for enhanced reductive dechlorination?

Optimal Dechlorination Conditions

- **Temperature 15–35 °C, with an optimum growth temperature between 25 and 30 °C**
- **pH 6.5 and 8.0**

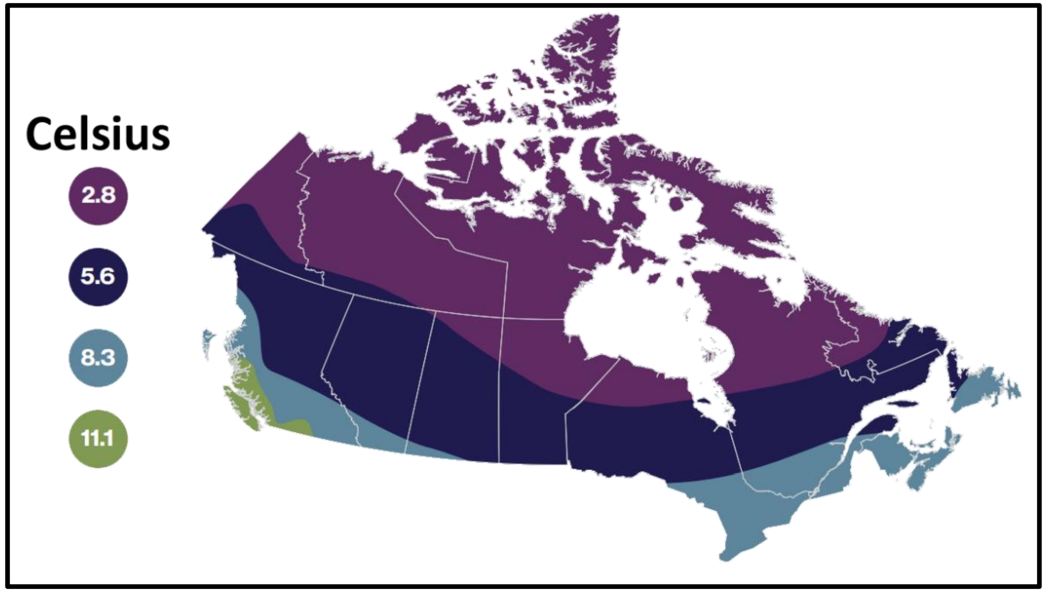
Groundwater Temperatures (°C)

Average shallow groundwater temperatures in the contiguous US

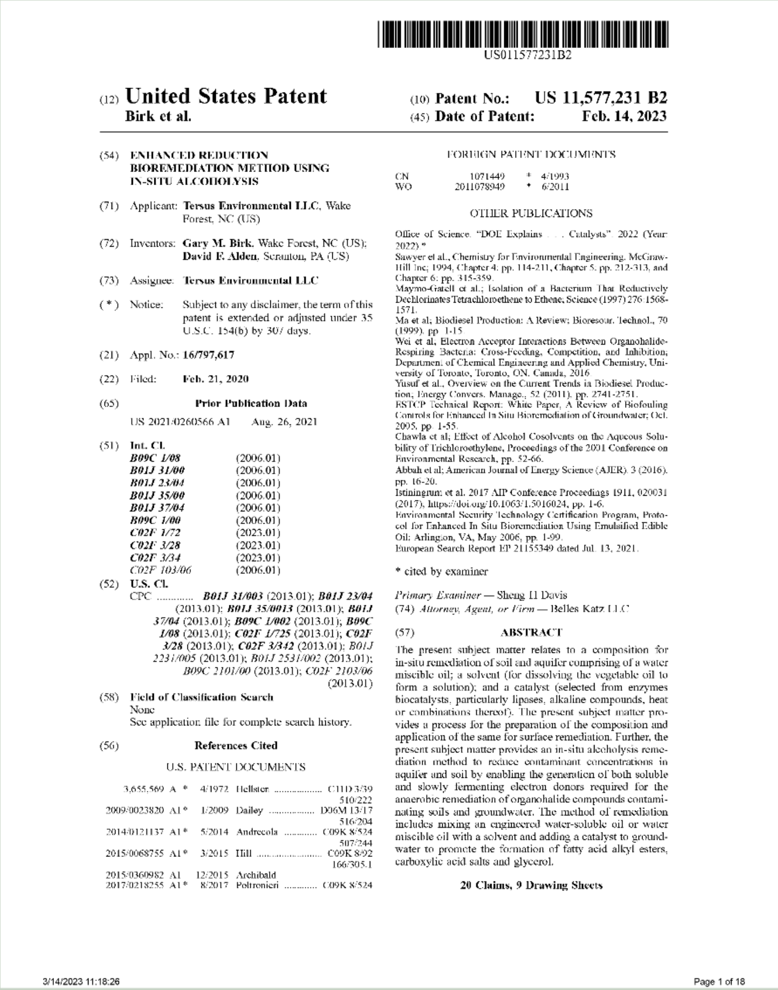


Ref: https://www.researchgate.net/publication/270565164, Derived from Collins [1925], Collins, W. D., 1925. Temperature of water available for industrial use in the United States: U. S. Geol. Survey Water-Supply Paper 520-F, p. 97-104.

Average shallow groundwater temperatures in Canada



Ref: Rinnai America Corporation, North America Ground Water Temperature Map



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

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

(54) **ENHANCED REDUCTION 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**

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 307 days.

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B01J 31/00	(2006.01)
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B01J 35/00	(2006.01)
B01J 37/04	(2006.01)
B09C 1/00	(2006.01)
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C02F 3/28	(2023.01)
C02F 3/34	(2023.01)
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(52) **U.S. Cl.**
CPC ***B01J 31/003*** (2013.01); ***B01J 23/04*** (2013.01); ***B01J 35/0013*** (2013.01); ***B01J 37/04*** (2013.01); ***B09C 1/002*** (2013.01); ***B09C 1/08*** (2013.01); ***C02F 1/725*** (2013.01); ***C02F 3/28*** (2013.01); ***C02F 3/342*** (2013.01); *B01J 2231/005* (2013.01); *B01J 2531/002* (2013.01); *B09C 2101/00* (2013.01); *C02F 2103/06* (2013.01)

(58) **Field of Classification Search**
None
See application file for complete search history.

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Primary Examiner — Sheng H Davis
(74) *Attorney, Agent, or Firm* — Belles Katz LLC

(57) **ABSTRACT**

The present subject matter relates to a composition for in-situ remediation of soil and aquifer comprising of a water miscible oil; a solvent (for dissolving the vegetable oil to form a solution); and a catalyst (selected from enzymes biocatalysts, particularly lipases, alkaline compounds, heat or combinations thereof). The present subject matter provides a process for the preparation of the composition and application of the same for surface remediation. Further, the present subject matter provides an in-situ alcoholysis remediation method to reduce contaminant concentrations in aquifer and soil by enabling the generation of both soluble and slowly fermenting electron donors required for the anaerobic remediation of organohalide compounds contaminating soils and groundwater. The method of remediation includes mixing an engineered water-soluble oil or water miscible oil with a solvent and adding a catalyst to groundwater to promote the formation of fatty acid alkyl esters, carboxylic acid salts and glycerol.

20 Claims, 9 Drawing Sheets

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Catalyzed Enhanced Reductive Bioremediation

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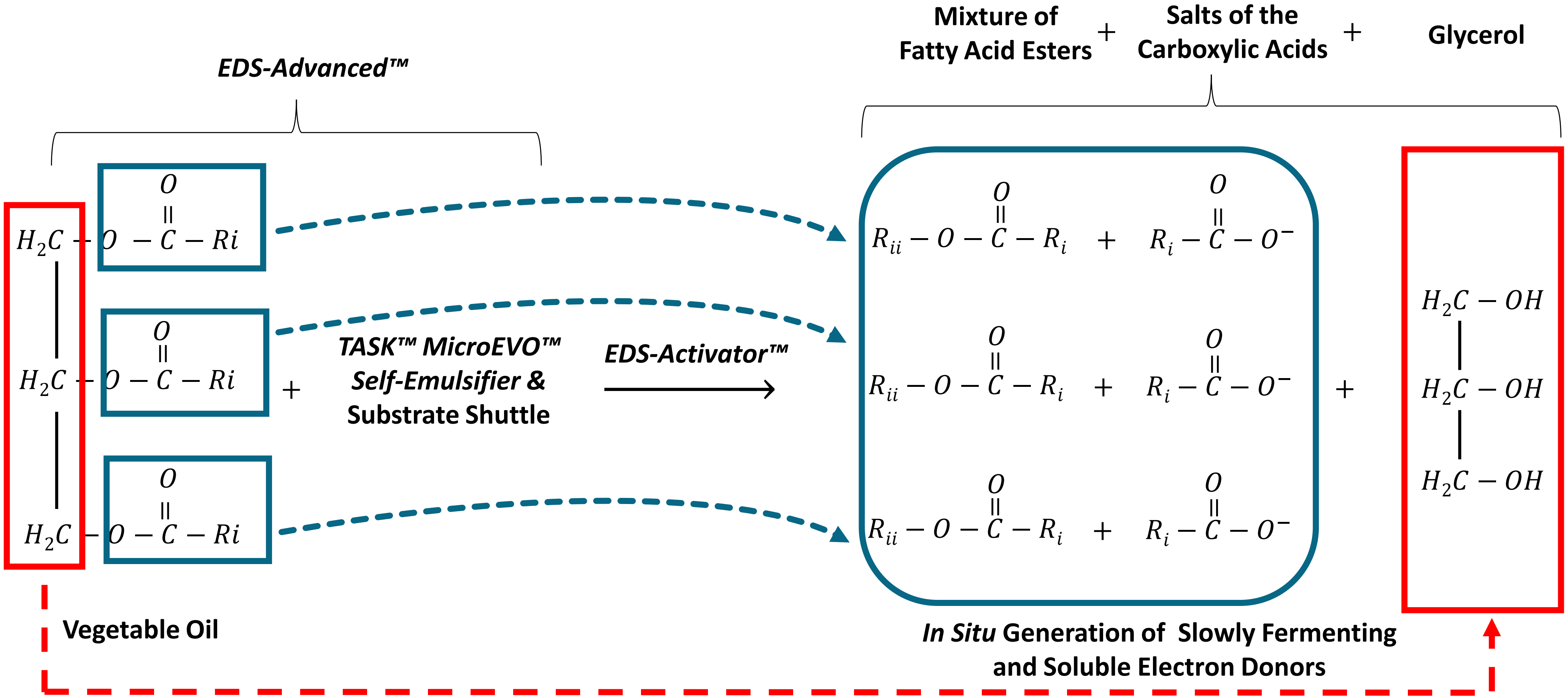
Definitions

- 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^-)

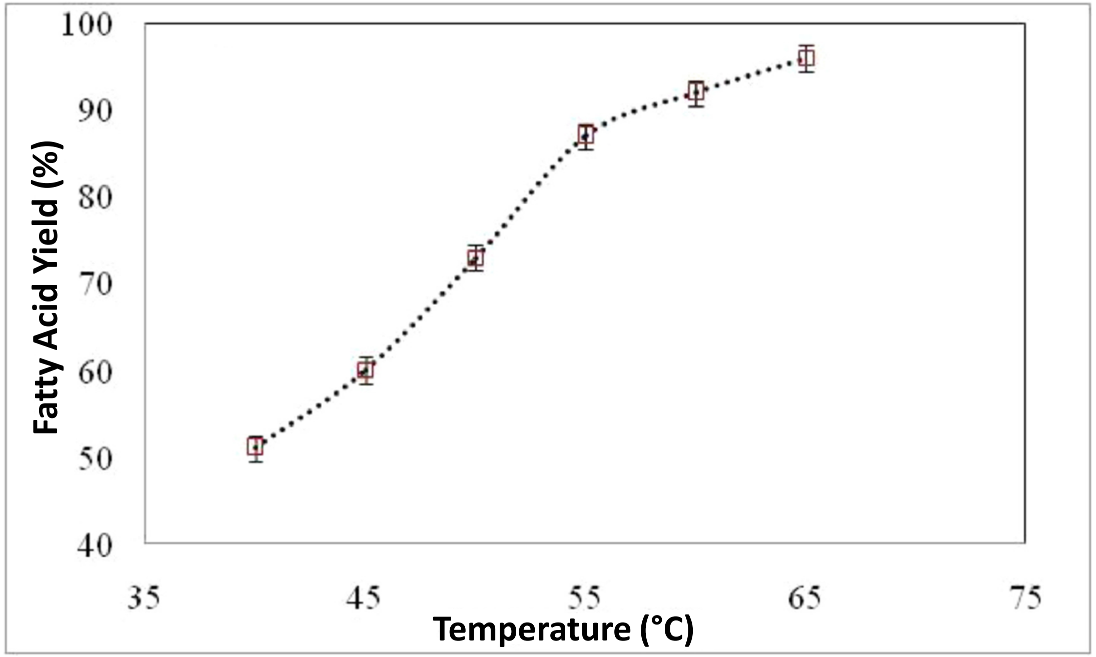
Lipase-catalyzed hydrolysis of triglyceride

- Biocatalyst
  - Enzyme (triglyceride lipases)

Temperature Effect on Yield

Homogeneous Alkaline Catalyst

- 1 wt.% Catalyst

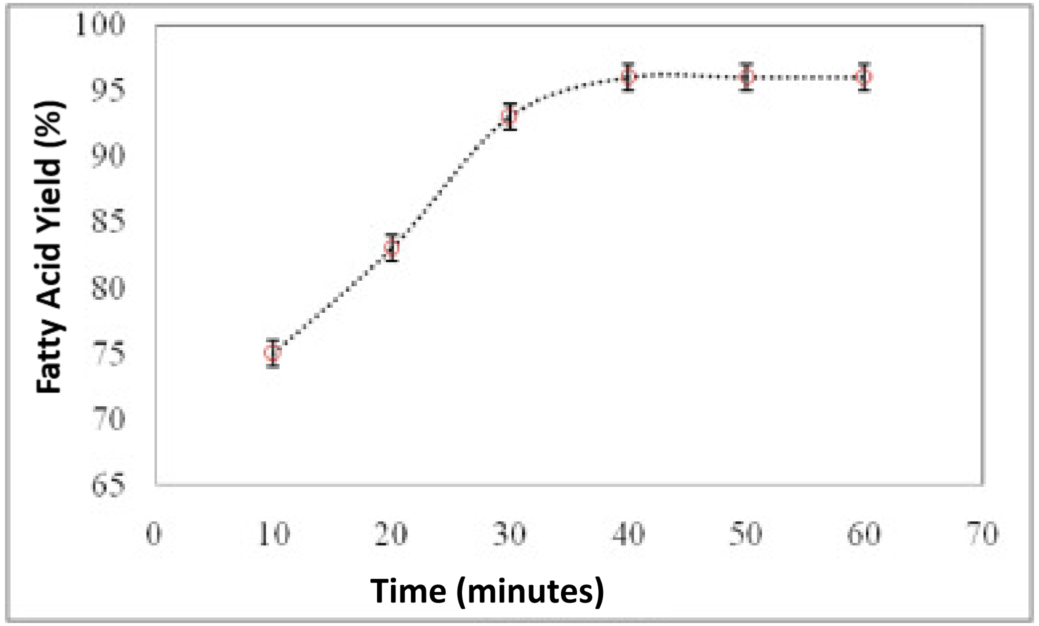


Modified from Kasirajan, Ramachandran. (2021). Biodiesel Production by two step process from an Energy Source of Chrysophyllum albidum Oil using Homogeneous Catalyst. South African Journal of Chemical Engineering. https://doi.org/10.1016/j.sajce.2021.05.011.

Effect of Reaction Time on Yield

Homogeneous Alkaline Catalyst

- 65°C of reaction temperature
- 1 wt.% Catalyst



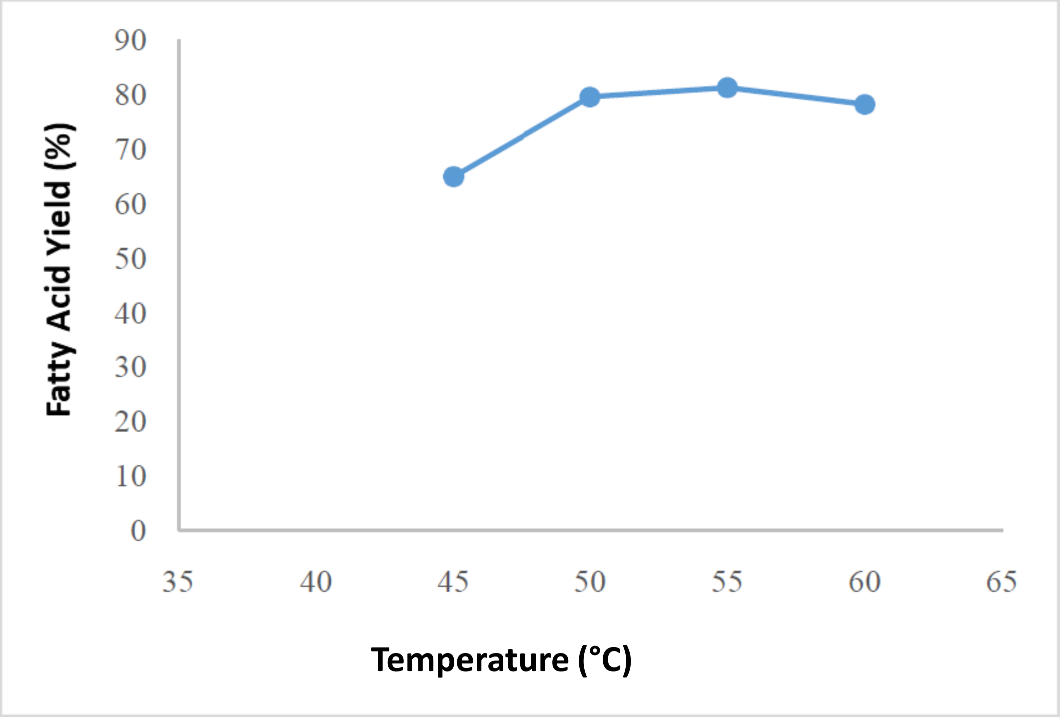
Modified from Kasirajan, Ramachandran. (2021). Biodiesel Production by two step process from an Energy Source of Chrysophyllum albidum Oil using Homogeneous Catalyst. South African Journal of Chemical Engineering. https://doi.org/10.1016/j.sajce.2021.05.011.

Temperature Effect on Yield

Enzyme (Lipase as Biocatalyst)

- Optimum at 55°C with the fatty acid yield of 81%

- Above 60°C , enzyme undergoes denaturation (loses structure)



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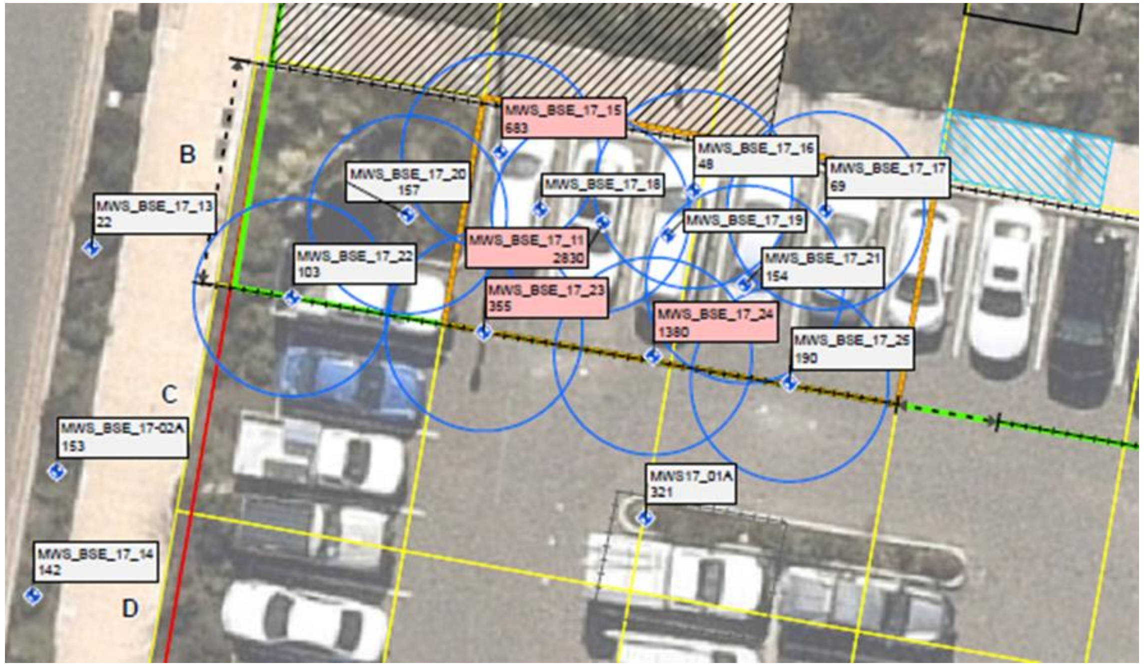
Example Projects

TCE Site

- 2,830 µg/L TCE (highest conc.)
- Primawave® Pressure Pulse
- Injected 75,000L of EDS-Advanced™ into the source zone over two weeks



Photos curtesy of Justin Kerr, Kerr Environmental, Greater Adelaide Area, SA, AUSTRALIA

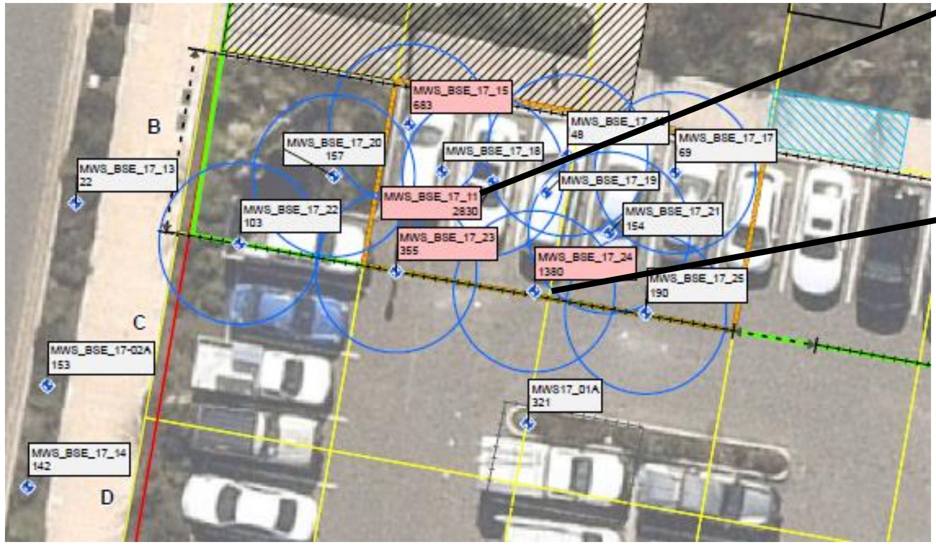
Injection Setup

Four injection lines with individual flow and pressure control and monitoring

Primawave® Pressure Pulse for injection into clays

Photos and video curtesy of Justin Kerr, Kerr Environmental, Greater Adelaide Area, SA, AUSTRALIA

TCE Results
(Approximately 95% mass reduction)

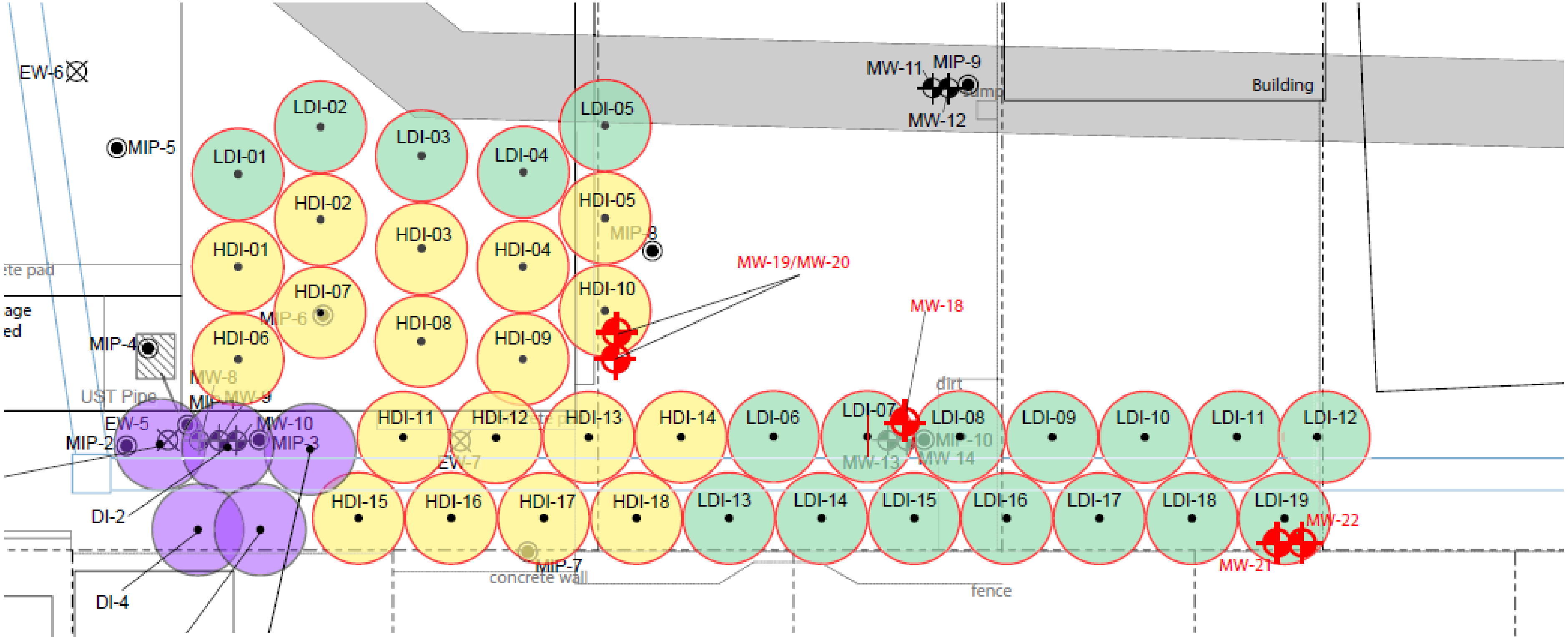


Data curtesy of Justin Kerr, Kerr Environmental, Greater Adelaide Area, SA, AUSTRALIA

MWS_BSE_17_11
Baseline 2,830 µg/L
Week 13 33.1 µg/L

MWS_BSE_17_24
Baseline 1,380 µg/L
Week 13 55.8 µg/L

TCE Site



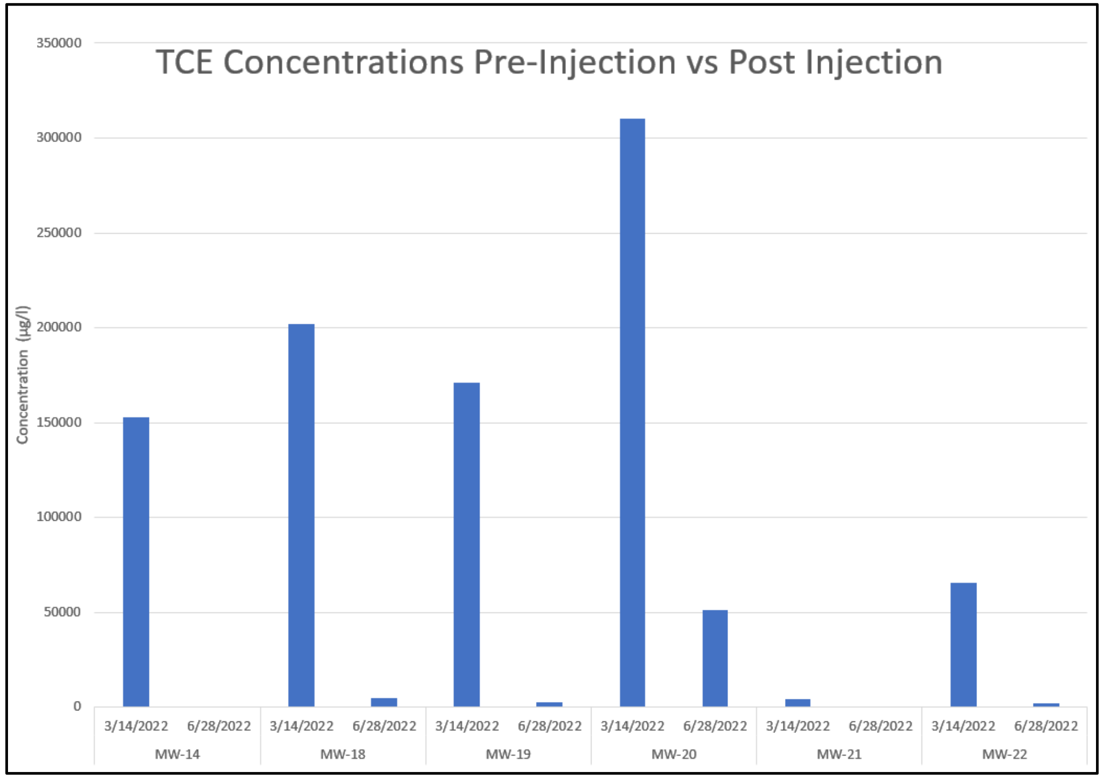
Yellow: High dose injections

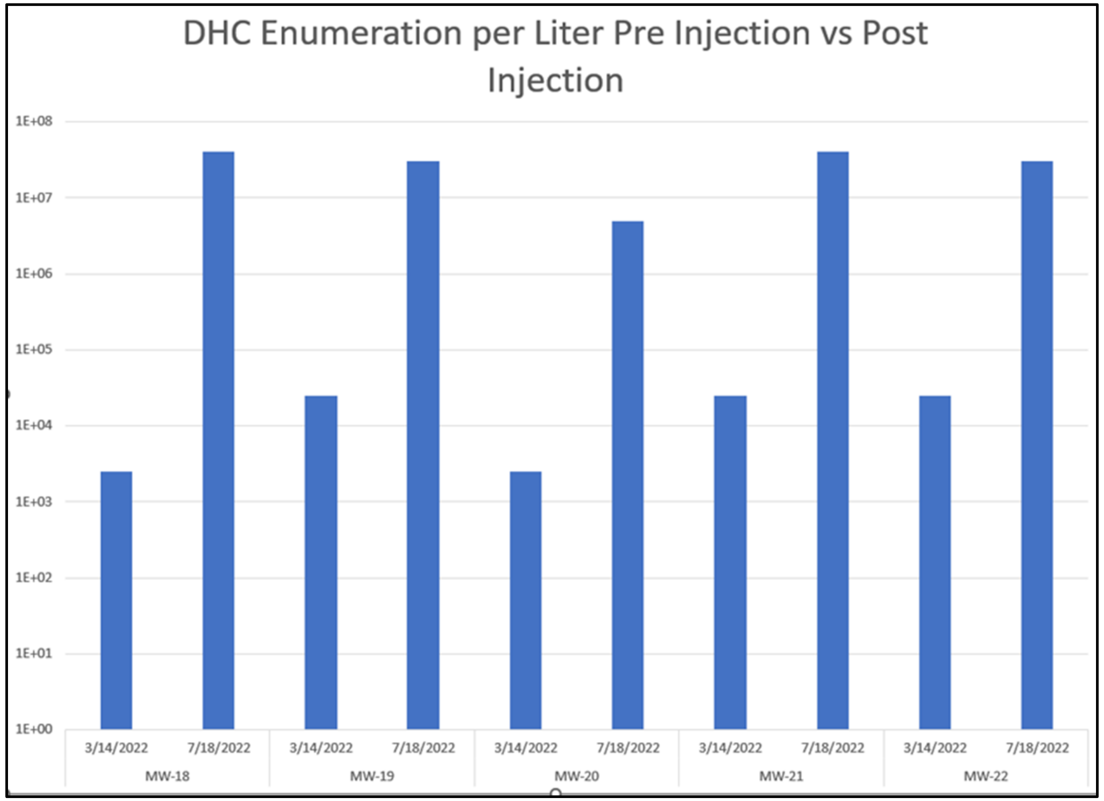
Green: Low dose injections

Purple: Low dose injections excluding KB-1®

Reference: Remediation Seminars Webinar, *How to Integrate Bench Scale Tests, Molecular Diagnostic Tools (MDT), and Compound-Specific Isotope Analysis (CSIA) to you Field Pilot Test*, Dec. 7, 2022

Injection Results





Reference: Remediation Seminars Webinar, *How to Integrate Bench Scale Tests, Molecular Diagnostic Tools (MDT), and Compound-Specific Isotope Analysis (CSIA) to you Field Pilot Test*, Dec. 7, 2022

Heat-Enhanced Catalyzed Reductive Bioremediation

Thermal Enhancement Options

Apply Heat

- Enhances transesterification reaction
- Reduces time from days to months to minutes to hours

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)

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 Fluid Injection

Hydrogeological parameters

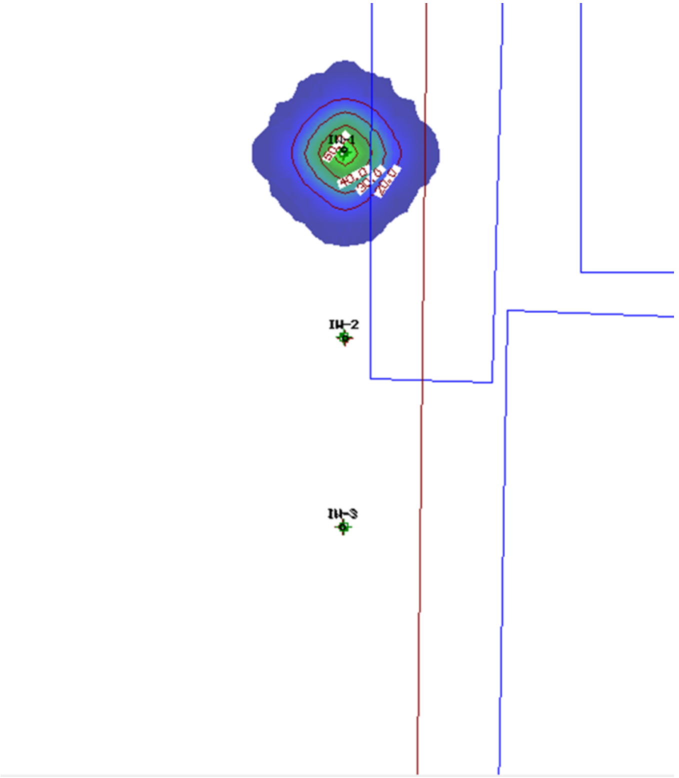
- Site lithology: sand
- Porosity: 0.33
- Aquifer hydraulic conductivity K of $1x10^{-2}$ cm/s
- Hydraulic gradient: 0.002 feet/feet

Injection

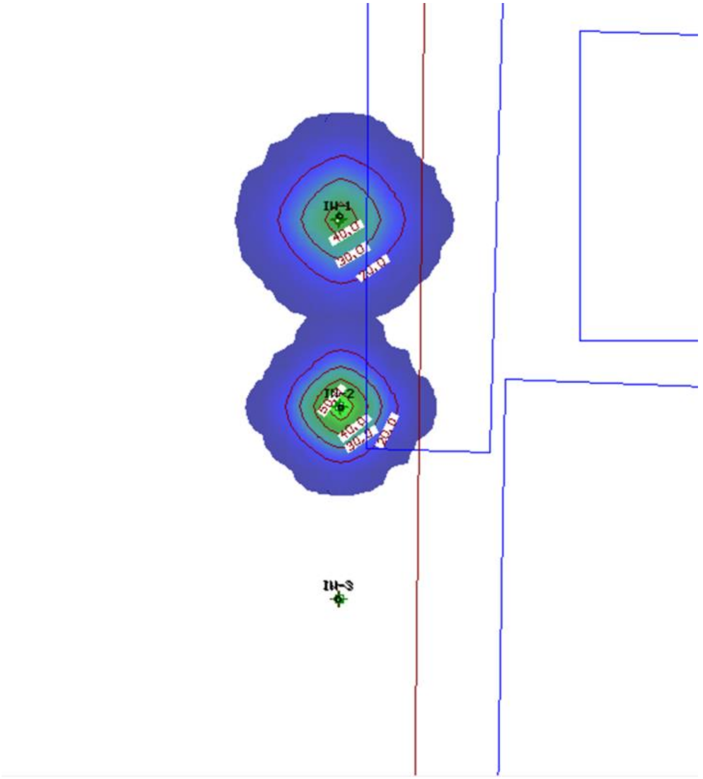
- 12-hour injection event
- 75 m^3 (19,813 gallons) of heated fluid to 90°C
- 150 m^3/d (27.5 gpm) flow rate

Model Results

Time = 0.5 days

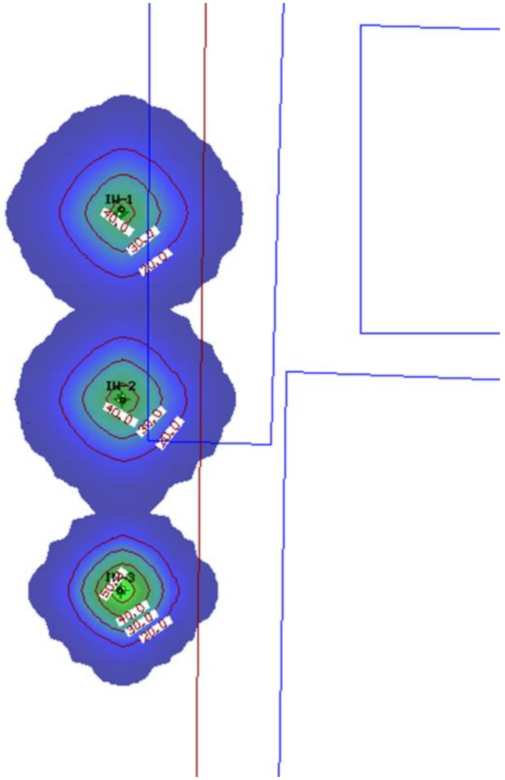


Time = 1 day

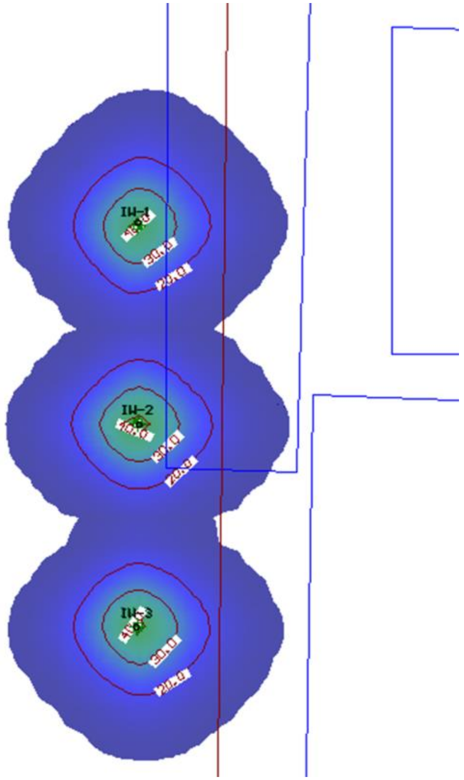


Model Results (continued)

Time = 1.5 days

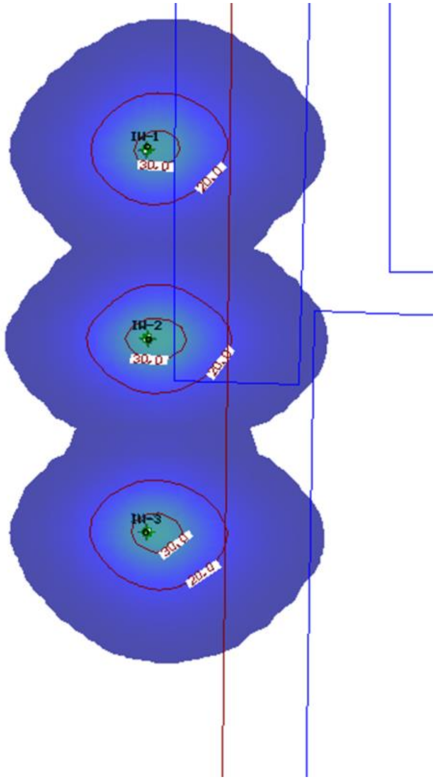


Time = 5 days

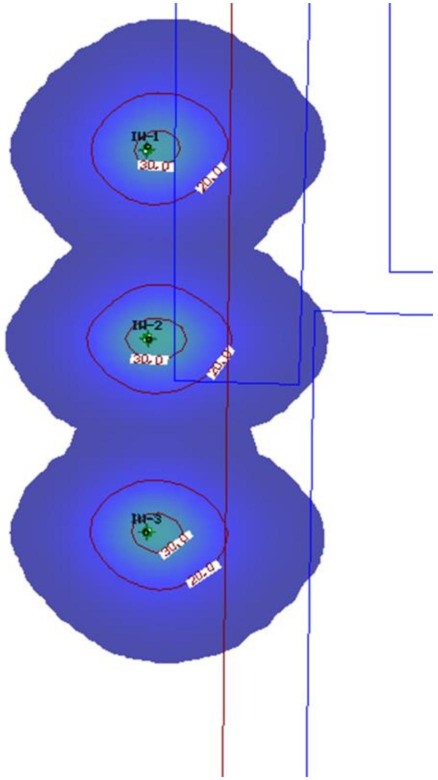


Model Results (continued)

Time = 10 days

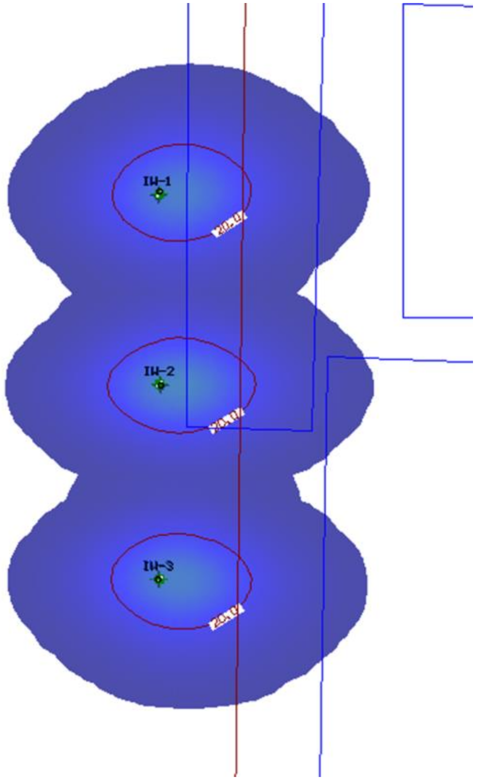


Time = 30 days

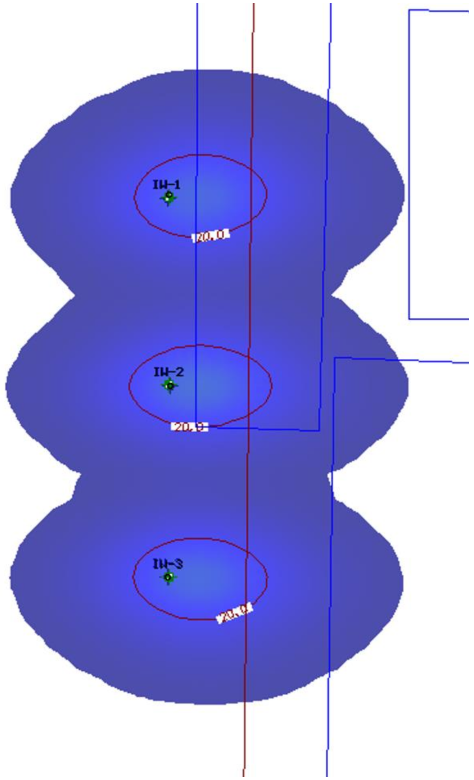


Model Results (continued)

Time = 60 days



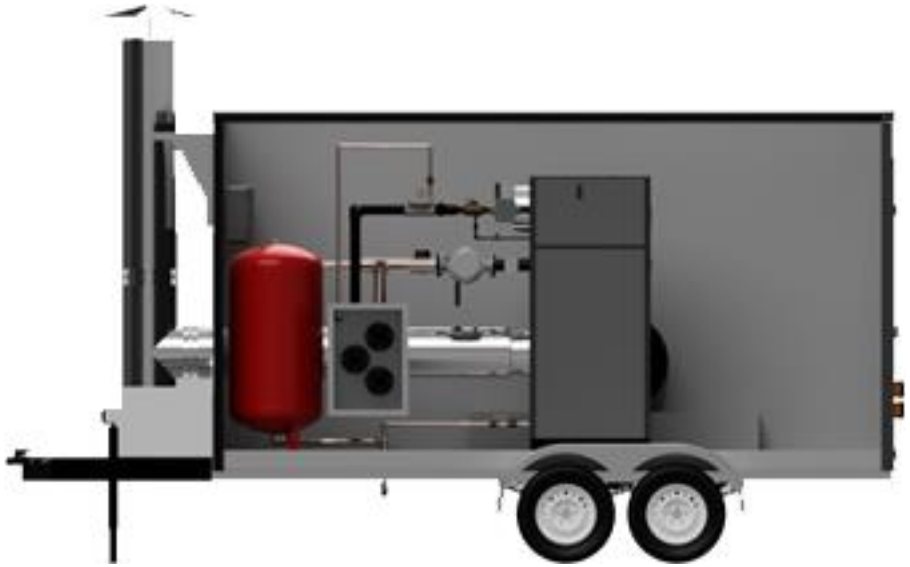
Time = 90 days

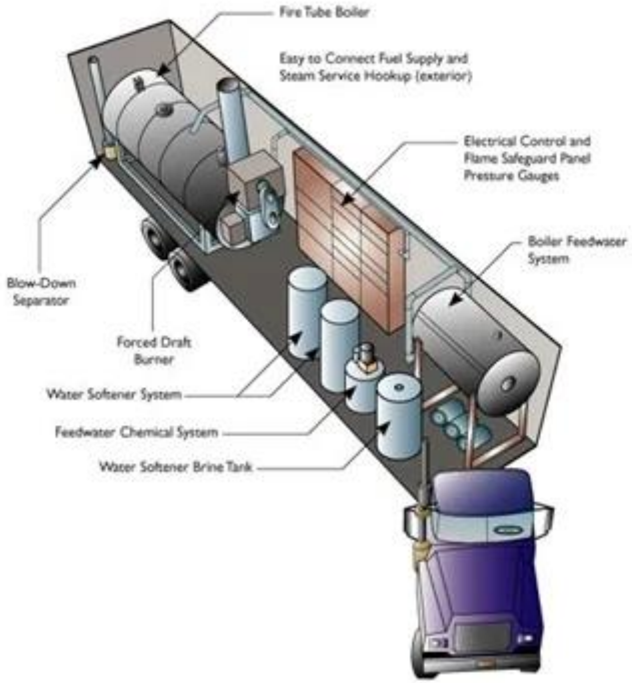


Hot Water Injections

- Insulated Semi Tank Trailer to haul 180-degree water
  - Delivery $7,900 / 6,000-gallon load
  - Demurrage $1,200/ 6,000 gallons

Mobile Boilers





Reference: Wilkinson Mobile Boilers, Inc.

Reference: Wilkinson Mobile Boilers, Inc.

Budgetary Cost Range

Rental

- Domestic/Heating Hot Water Mobile Boiler
  - Monthly Rental: ~ $12K
  - Cleanup Fee: ~$3k
- Hot Water Storage Tank
  - Monthly Rental: ~ $3.5K
  - Cleanup Fee: ~$3k
- Freight: $4 to $6K each way

Turn-key (24-hour day)

Description	Est. Unit Rate
4 Man Crew Mobilize to site	$10,000
Day crew, 2 Operators/Technicians	$3,250/shift
Night crew, 2 Operators/Technicians	$3,250/shift
Boiler, Mobile unit w/ 80' of Hose $725.00/ Hour x 24-hour day	$17,400/day
Boiler Fuel Surcharge $55.00 x 24-hour day	$1,320/day
Per Diem x 4 Guys per night	$1,250/night
4 Man Crew Demobilize	$8,500

Photograph Curtesy of Corporativo SIRN S de RL de CV

Tankless Heaters

Water Heating Capacity Data		
Temperature Rise (°F)	Temperature Rise (°C) ΔT°C = 5/9 ΔT°F	Flow Rate (GPM)
35	19.4	12.1
45	25.0	9.4
55	30.6	7.7
65	36.1	6.5
75	41.7	5.6
90	50.0	4.7
100	55.6	4.2
120	66.7	3.5
140	77.8	3.0

Potential Reaction Temp of ~30 to 40°C (rows 65–100 °F)

Heat Enhanced Reductive Bioremediation

- Microbes that do all the work like a warm environment

- Warm water has lower dissolved gases

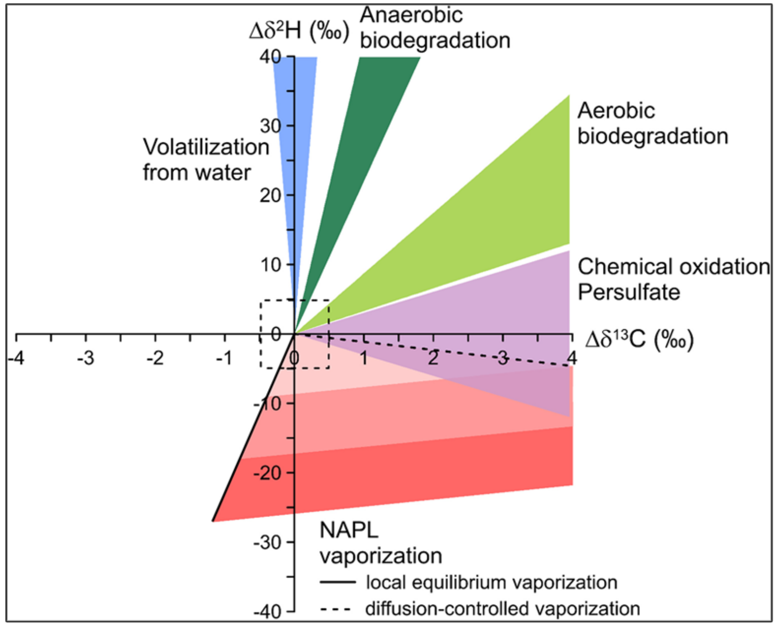
- Heating increases transesterification reaction rates

Performance Monitoring

Key Monitoring Tools

- Volatile Fatty Acids (VFAs)
- Next-Generation Sequencing (NGS)
- Compound-Specific Isotope Analysis (CSIA)

Photograph Curtesy of SiREM Lab



Ref: Groundwater Monitoring Rem, Volume: 38, Issue: 4, Pages: 88-98, First published:04 September 2018, DOI: (10.1111/gwmr.12300)

Thank you

tersus environmental

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

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