Remediation Seminar

Advances in EVO Deployment Using *In Situ* Alcoholysis

Effective Bioremediation of Chlorinated Solvent Sites – Avoiding Pitfalls and Maximizing Performance

Part 1, Wednesday, April 28, 2021

tersus environmental

Agenda

01 Bioremediation
Biological Reductive Dechlorination

02 Electron Donors
Overview and Options

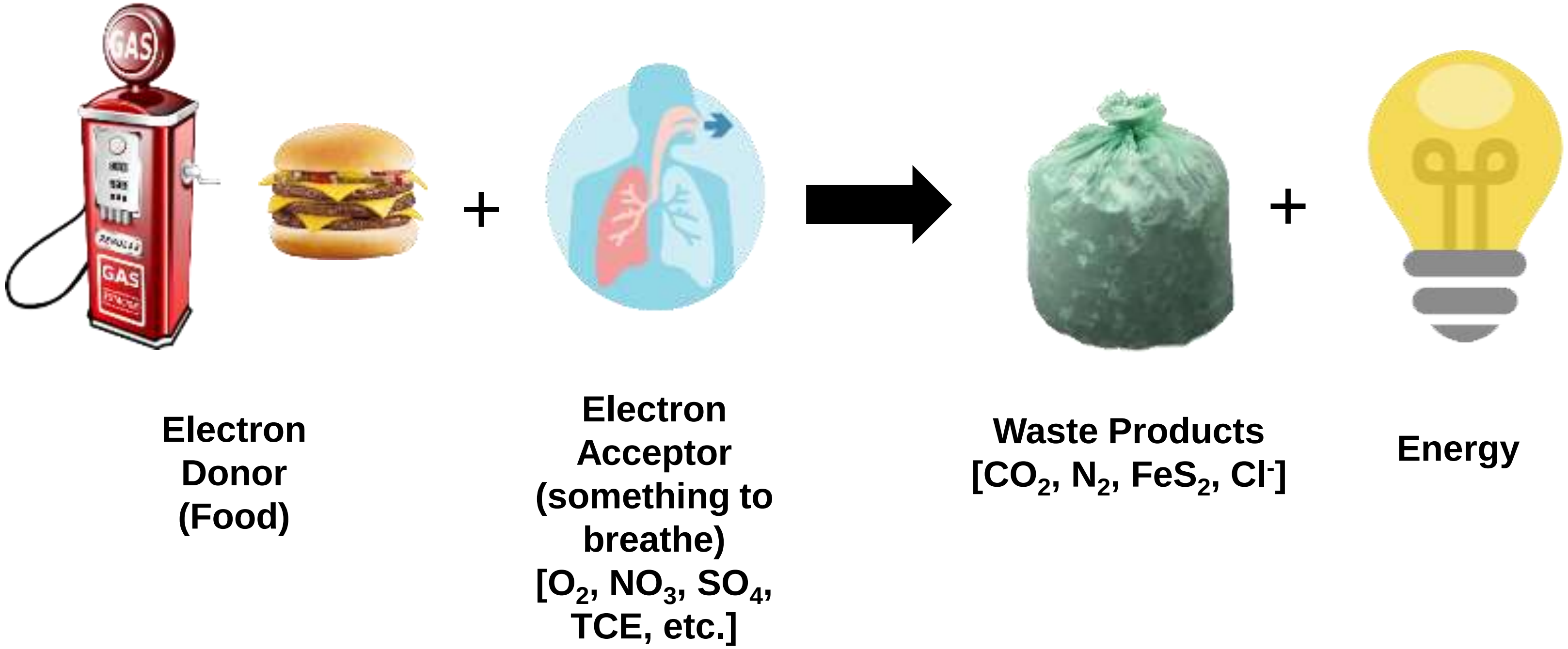
03 Emulsified Vegetable Oils
History and Advancements

04 pH
Impact of pH on Dechlorination

05 Bio-Fouling
Why do Wells Bio-Foul?

06 Subsurface Distribution
Method for Improved ROI and Fatty Acid Distribution

How Does Bioremediation Work?

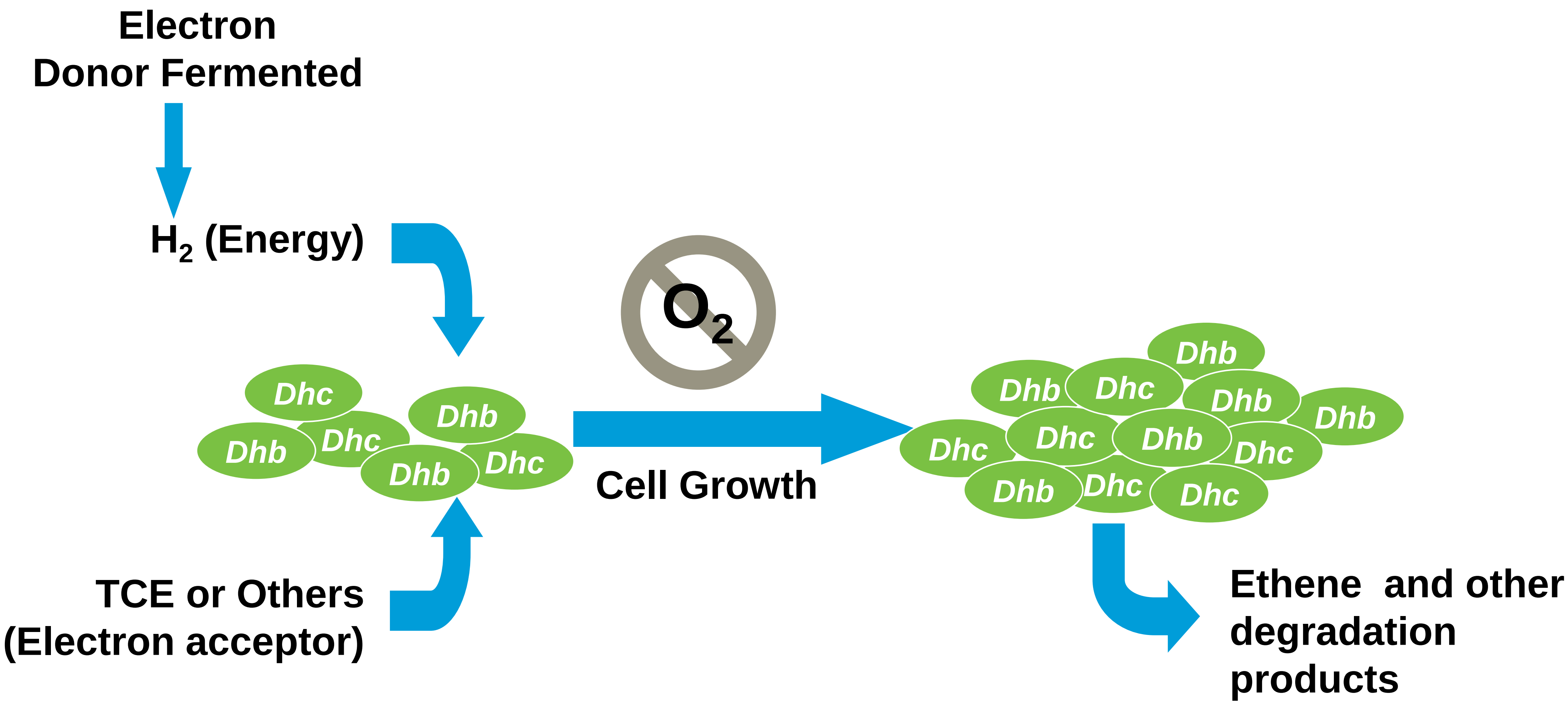


(Drawing Modified from AFCEE and Wiedemeier)

What is needed?

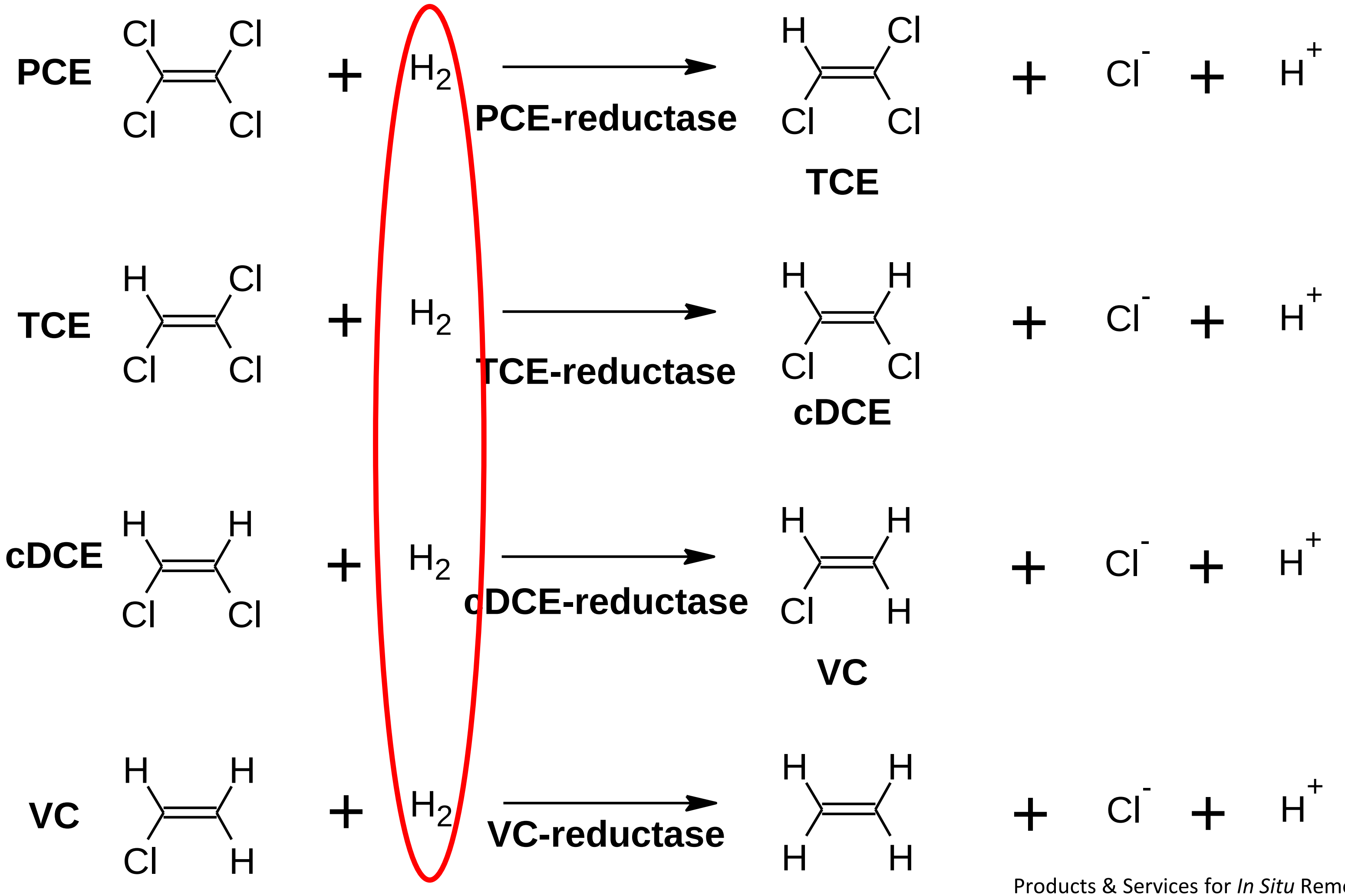
- Organic substrates that ferment to:
  - Acetate
  - Hydrogen (H_2)
- Strong reducing conditions
- Right organohalide respiring bacteria
- Nutrients

Biological Reductive Dechlorination



Slide Courtesy of SiREM

Reductive Dechlorination by Dhc



Ethene


Anaerobic Fermentation
Soybean oil ferments to acetic acid and hydrogen

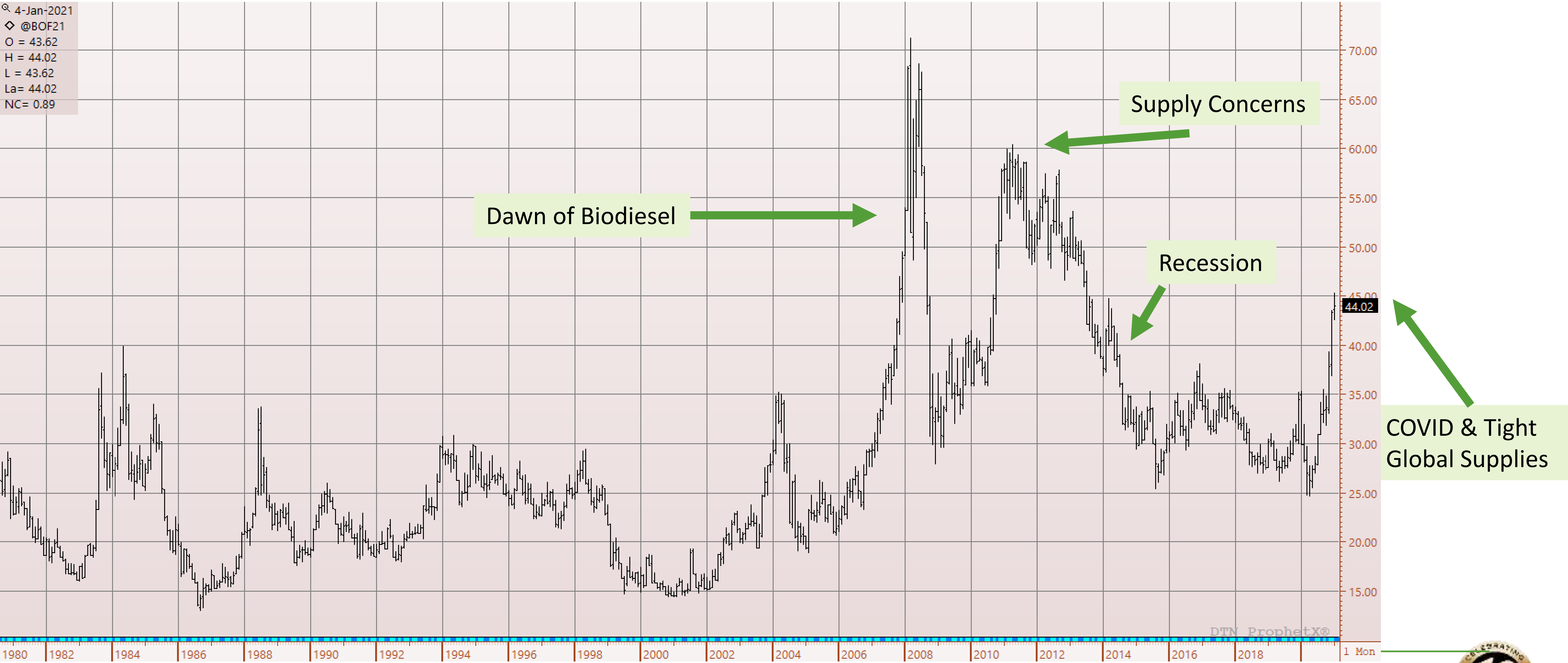
Electron Donors

Average Composition and Electrons Released During Anaerobic Fermentation

Electron Donor	Atoms per Mole Substrate			Average Molecular Weight	H_2 Released per mole Substrate	Moles H_2 Released per gram Substrate
	Carbon	Hydrogen	Oxygen			
Acetate	2	4	2	60.1	4	0.0666
Lactate	3	6	3	90.1	6	0.0666
Glucose	6	12	6	180.2	12	0.0666
Soybean Oil	56.3	99.5	6	873.1	156.5	0.1792

Ref: ESTCP, May 2006, Table 2.3

A Historic Look at Soybean Oil Prices



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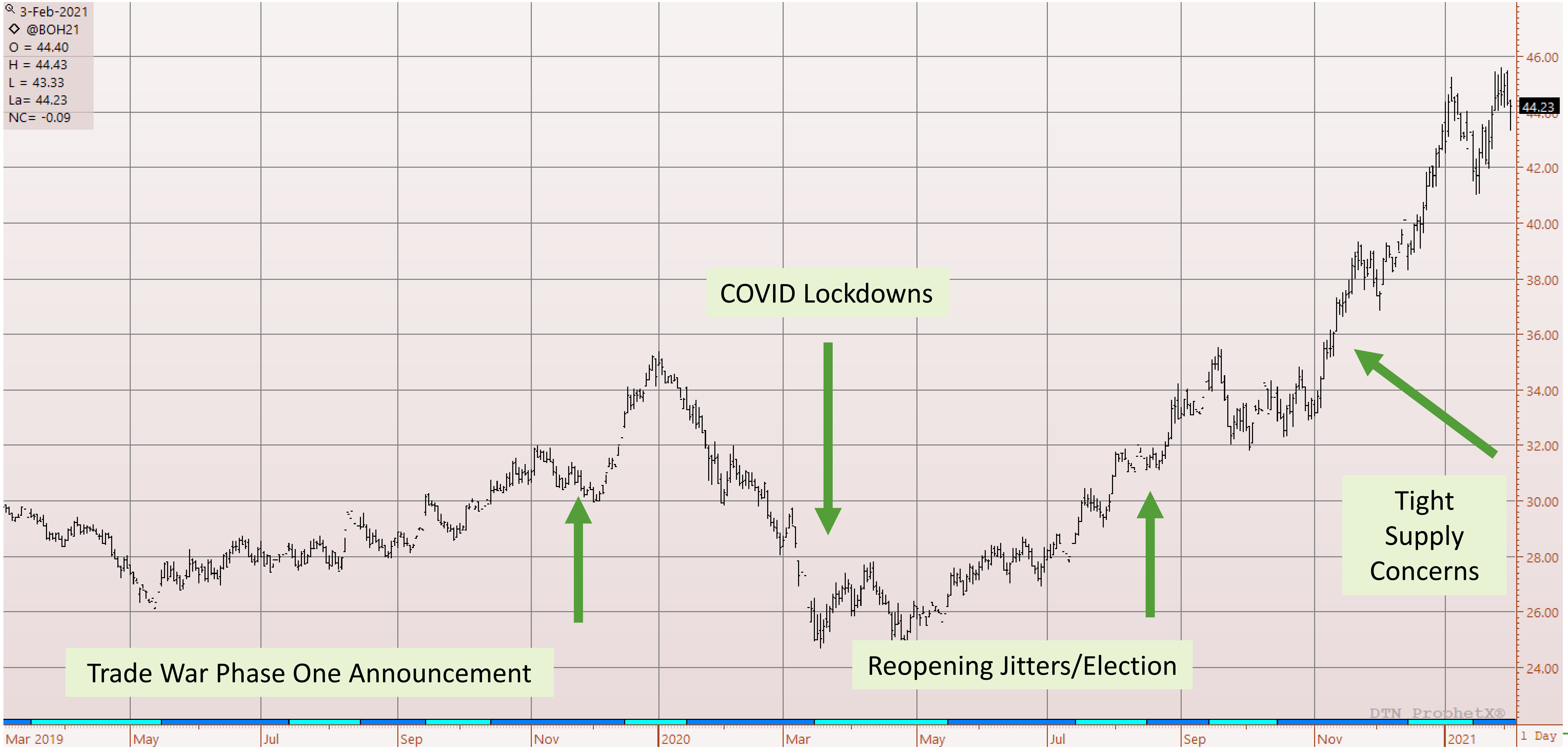
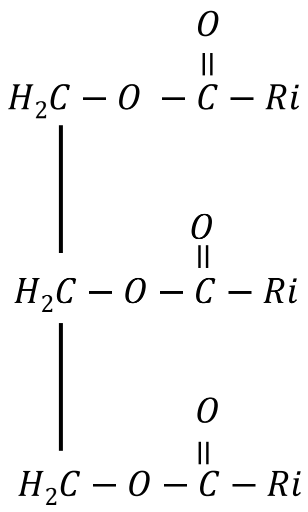
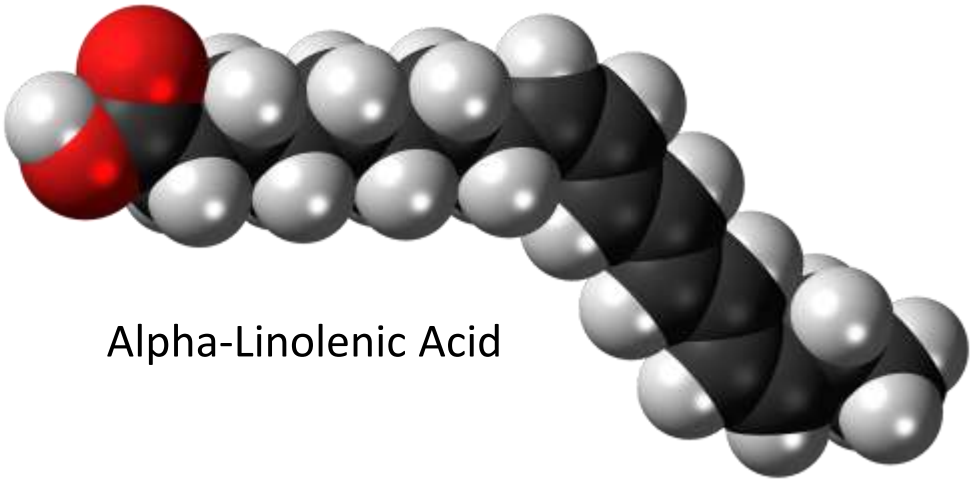
Nearby Continuous Soybean Oil Chart (02.03.2021)



Soybean Fatty Acid Distribution

Fatty Acid		Percent
C-16:0	Palmitic	11.0 %
C-18:0	Stearic	4.0 %
C-18:1	Oleic	24.0 %
C-18:2	Linoleic	54.0 %
C-18:3	Linolenic	7.0 %

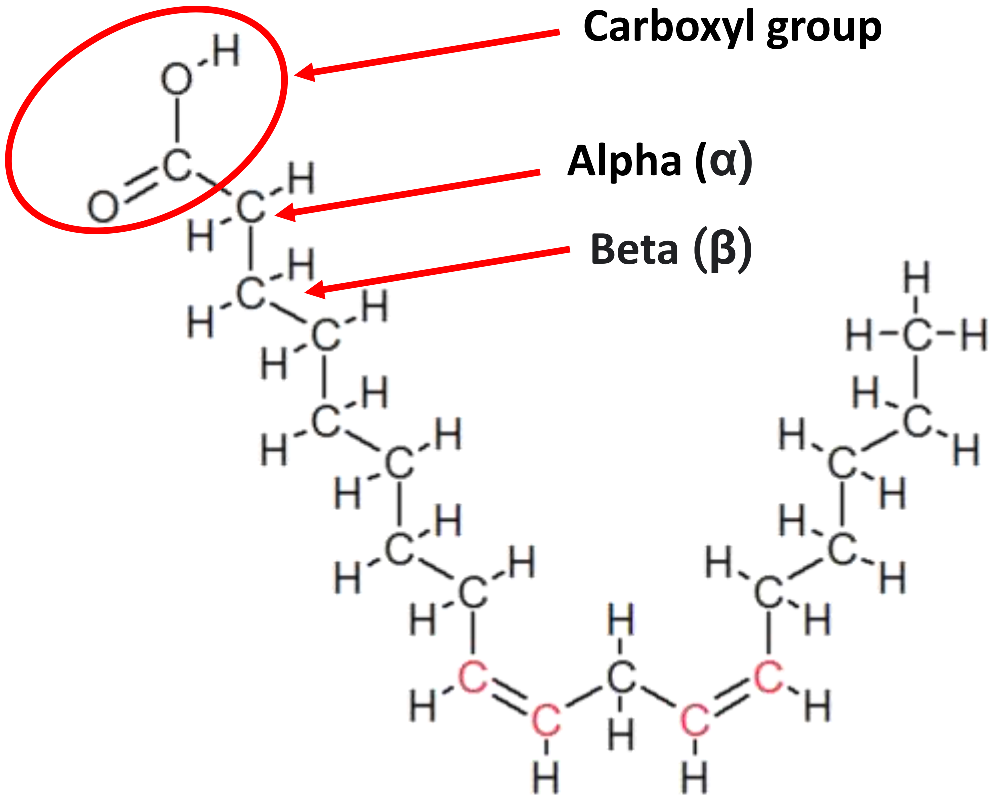




Alpha-Linolenic Acid

Fatty Acid Oxidation

Linoleic Acid



Multiple step metabolic process

$$C_nH_{2n}O_2 + 2\ H_2O \Rightarrow C_{n-2}H_{2n-4}O_2 + 2\ H_2 + C_2H_4O_2$$

- Removes two carbons from the chain
- Releases:
  - Four hydrogen atoms (H)
  - Acetic Acid ($C_2H_4O_2$)

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.

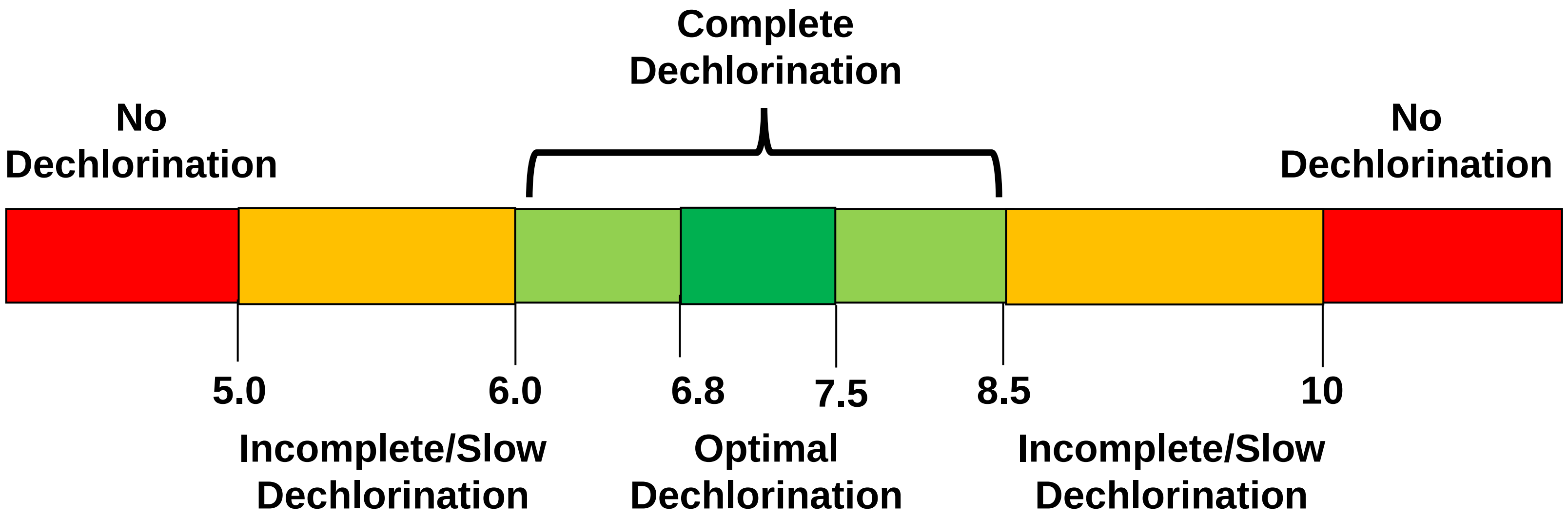
- Rapid consumption
- Does not migrate beyond injection zone
- Required for cDCE -> VC -> ethene

pH Plays a Key Role in VFA Production

Systems under alkaline conditions

- Enhances the activity of fatty acid-producing bacteria
- Inhibits methanogens
- Increases production of VFAs

Impact of pH on Dechlorination

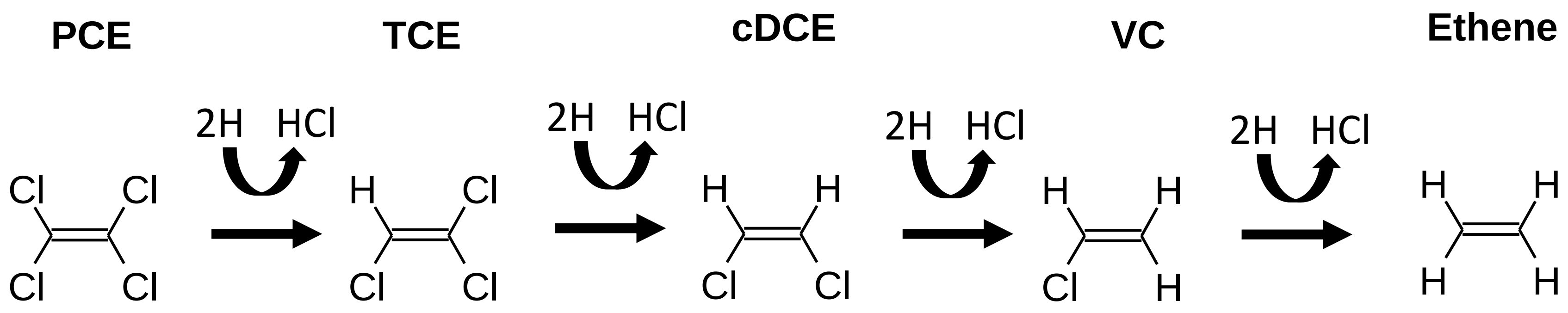


- pH of 6.0-8.5 is generally required for dechlorination to ethene*
- pH 6.8-7.5 is considered optimal range, 7.5 is best*
- Sites with low pH more likely to accumulate cDCE/VC

*Rowlands, 2004 (Slide Courtesy of SiREM)

Why is low pH so Common?

- Some sites have intrinsic groundwater pH in the 5.0-6.0 range
- Reductive dechlorination produces hydrochloric acid



Fermentation of electron donors generates acidic byproducts

Lactic Acid

- $2H_2$ + Acetate + CO_2
- CO_2 dissolves in water forming carbonic acid

Biofouling

Nutrients in the vicinity of aerobic wells promote excessive biomass growth that reduce permeability

Bacterial growth within delivery wells

Hard Soap and Soap Scum

Saponification

The Process of Making Soap

\+

=

Acid
(Oil)

Base
(Lye)

Salt
(Soap)

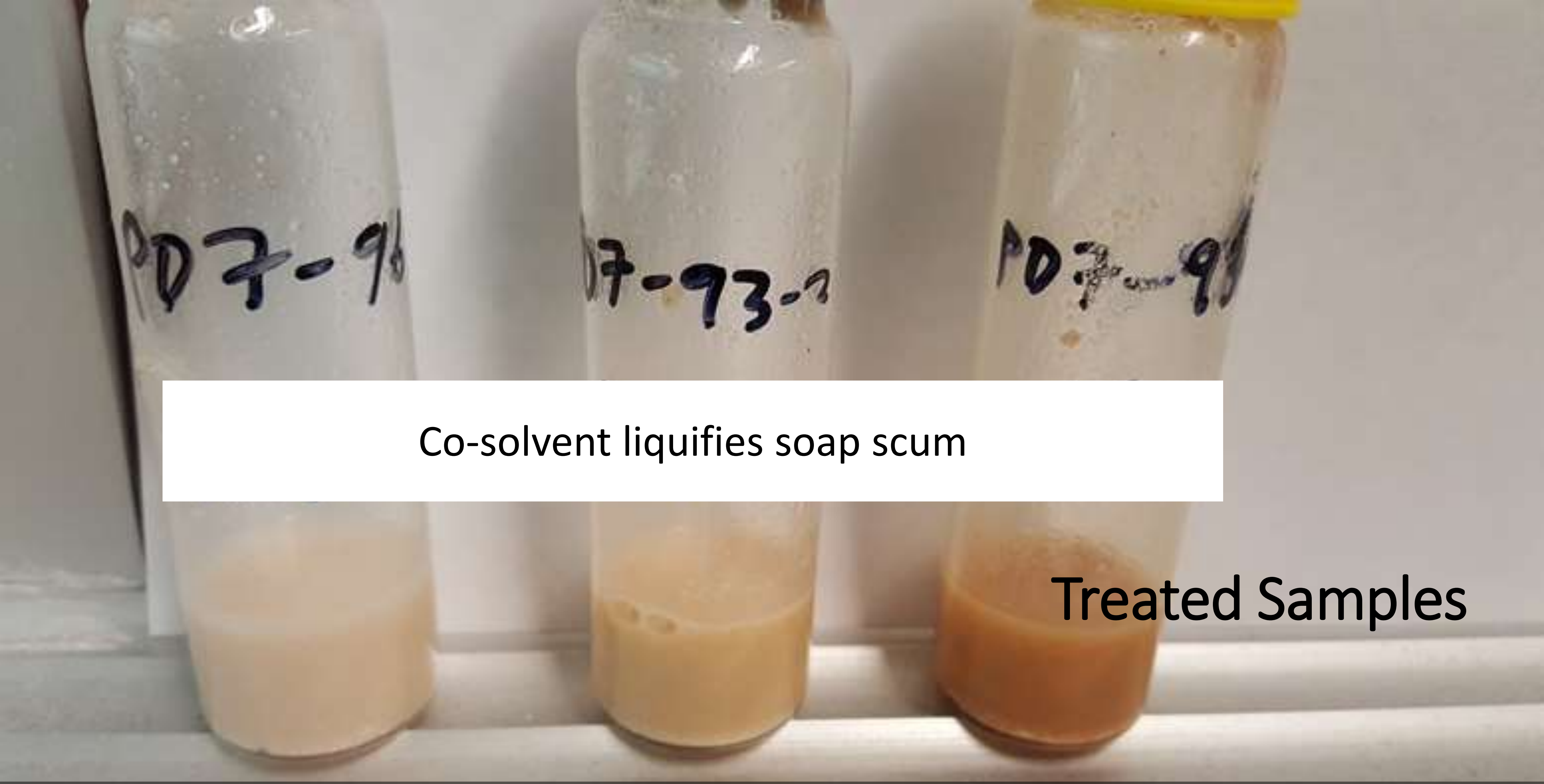
Hard Water

- Water that contains salts of calcium and magnesium principally as:
  - Bicarbonates
  - Chlorides
  - Sulfates
- Ferrous iron may also be present

Hard Water

Calcium and Magnesium Ions

- React with the fatty acids to form an insoluble gelatinous curd



Co-solvent liquifies soap scum

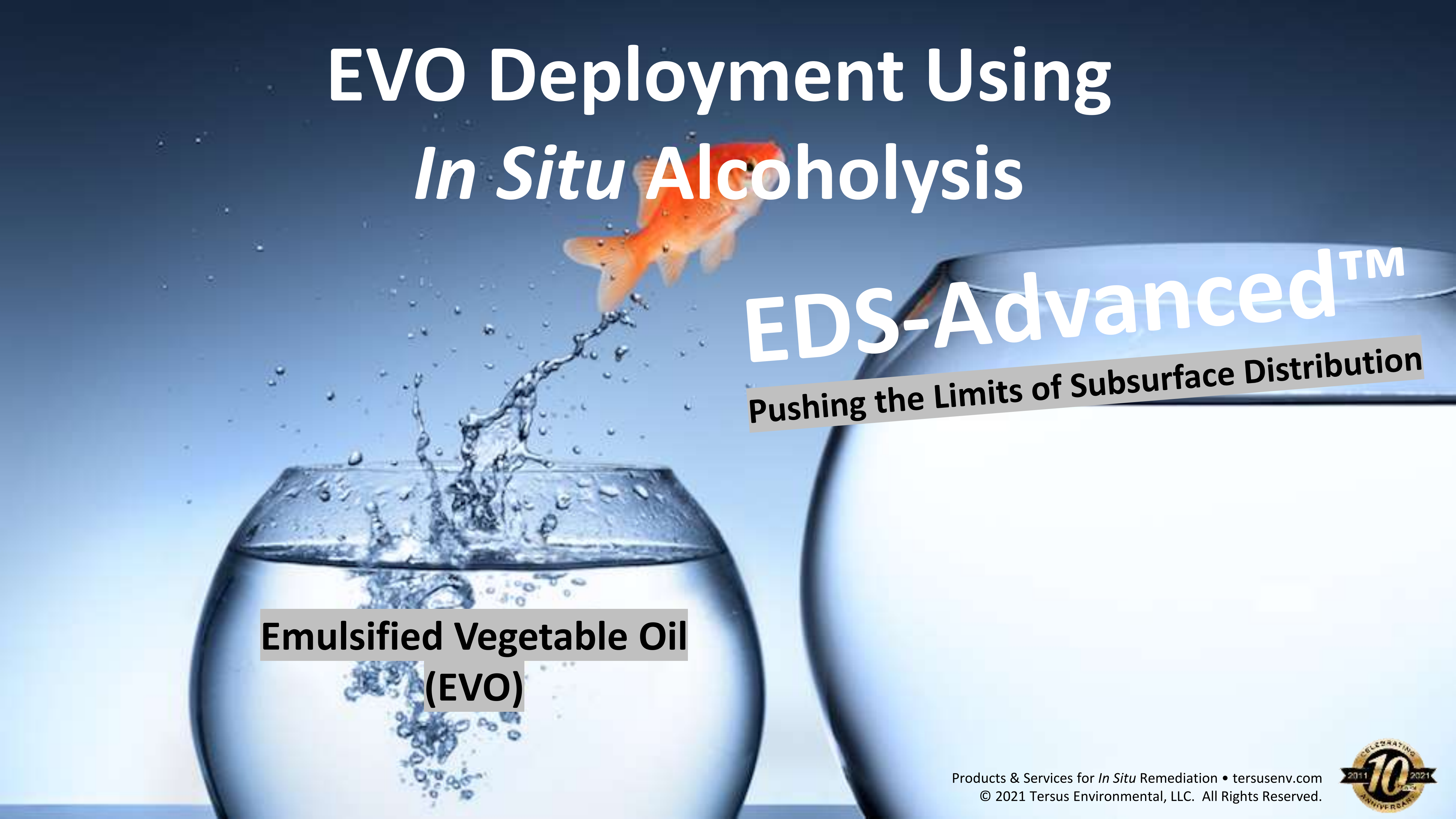
Treated Samples

Alkaline Groundwater

Bench test to liquify viscous material

- Samples mixed with co-solvent liquifies insoluble gelatinous curd
- Addition of water, forms an EVO

EVO Deployment Using *In Situ* Alcoholysis

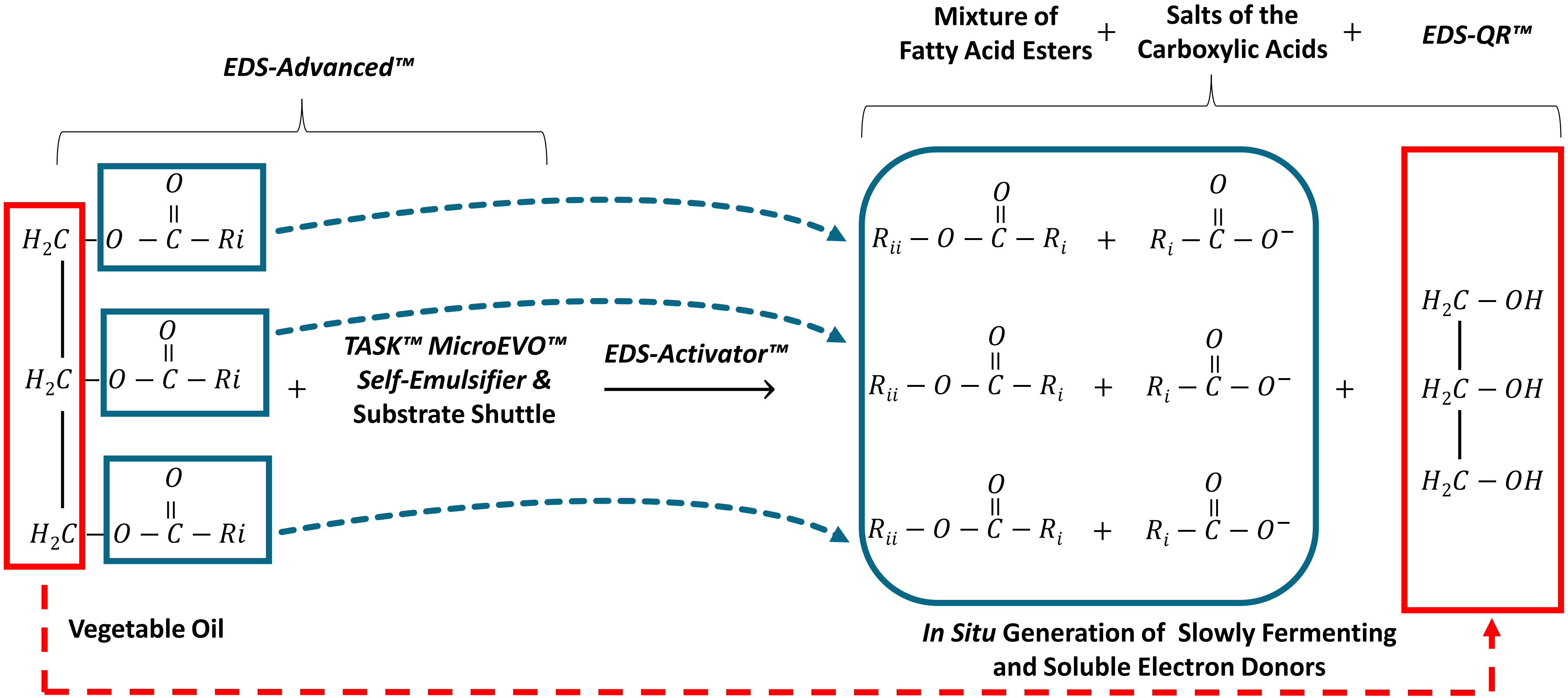


EDS-Advanced™

Pushing the Limits of Subsurface Distribution

Emulsified Vegetable Oil (EVO)

Anaerobic Bioremediation Deploying Electron Donor Via *In Situ* Alcoholysis



Activator Options

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

- Heat
  - Steam hydrolysis
  - Electrical resistance heating
  - Thermal conduction heating
  - Gas thermal heating
  - Residual heat from an in-situ thermal remediation project

- Biocatalyst
  - Enzyme (triglyceride lipases)

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

Typical Application Rates

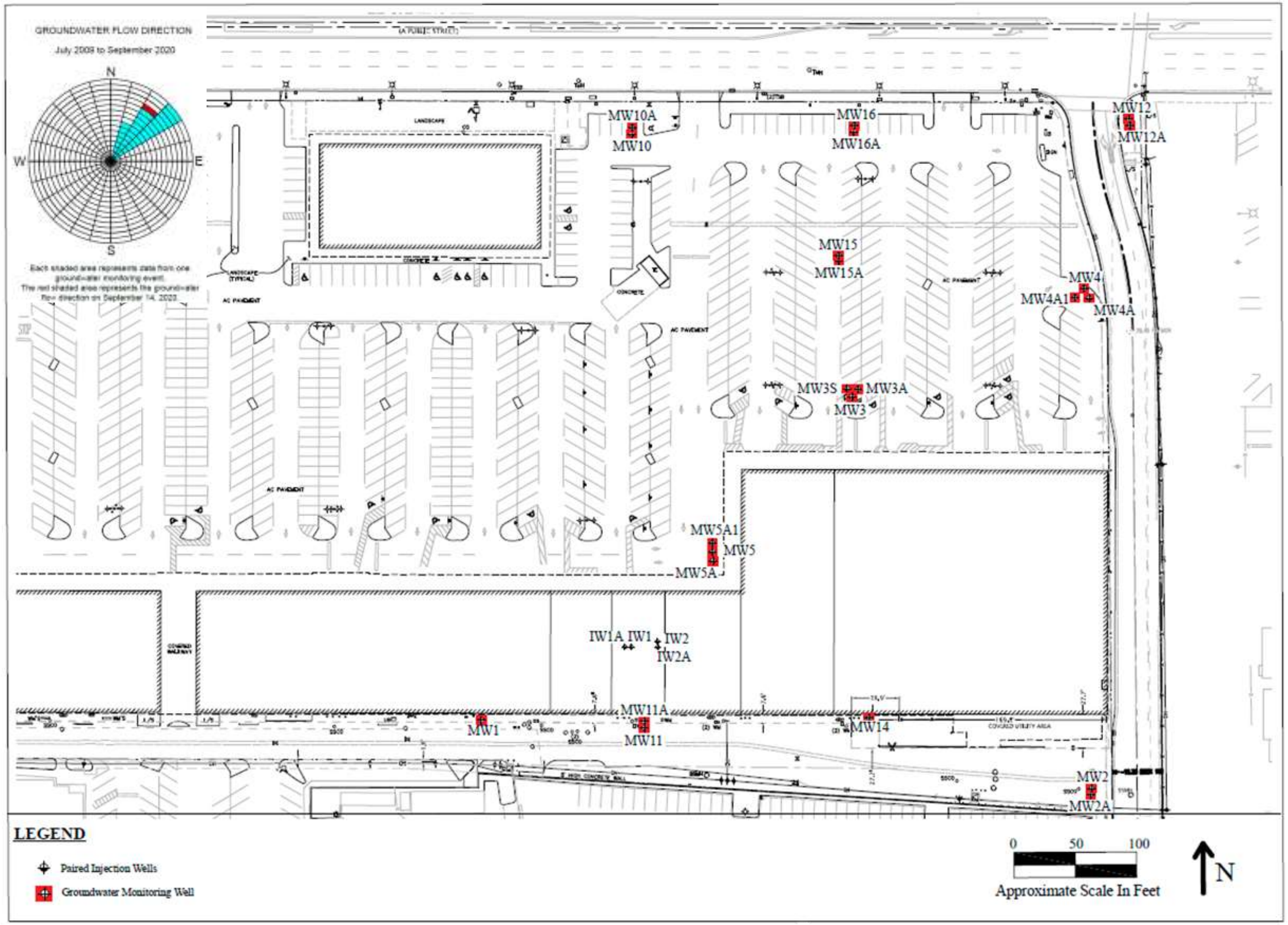
EDS-ER™ (Soybean Oil and TASK™ MicroEVO™ Self-Emulsifier	2 to 8 g/L
EDS-Activator™	16 to 20% of EDS-ER Dose
EDS Substrate Shuttle (Co-Solvent)	0 to 0.4 g/L
mZVI Suspension	4 to 6 g/L

ZVI with Biostimulation and Bioaugmentation

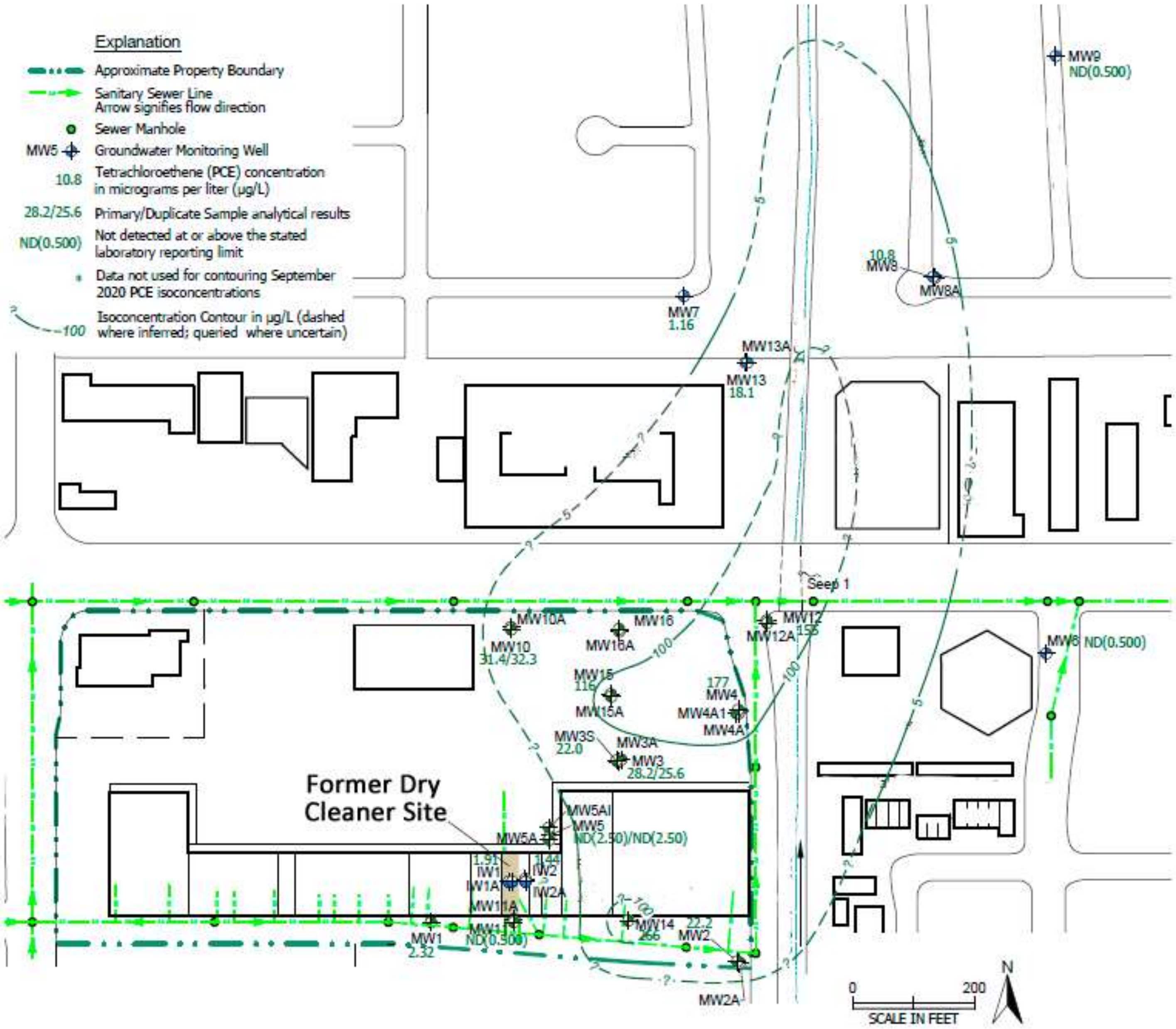
Case Study

Former Dry Cleaner Site

Former Dry Cleaner Site

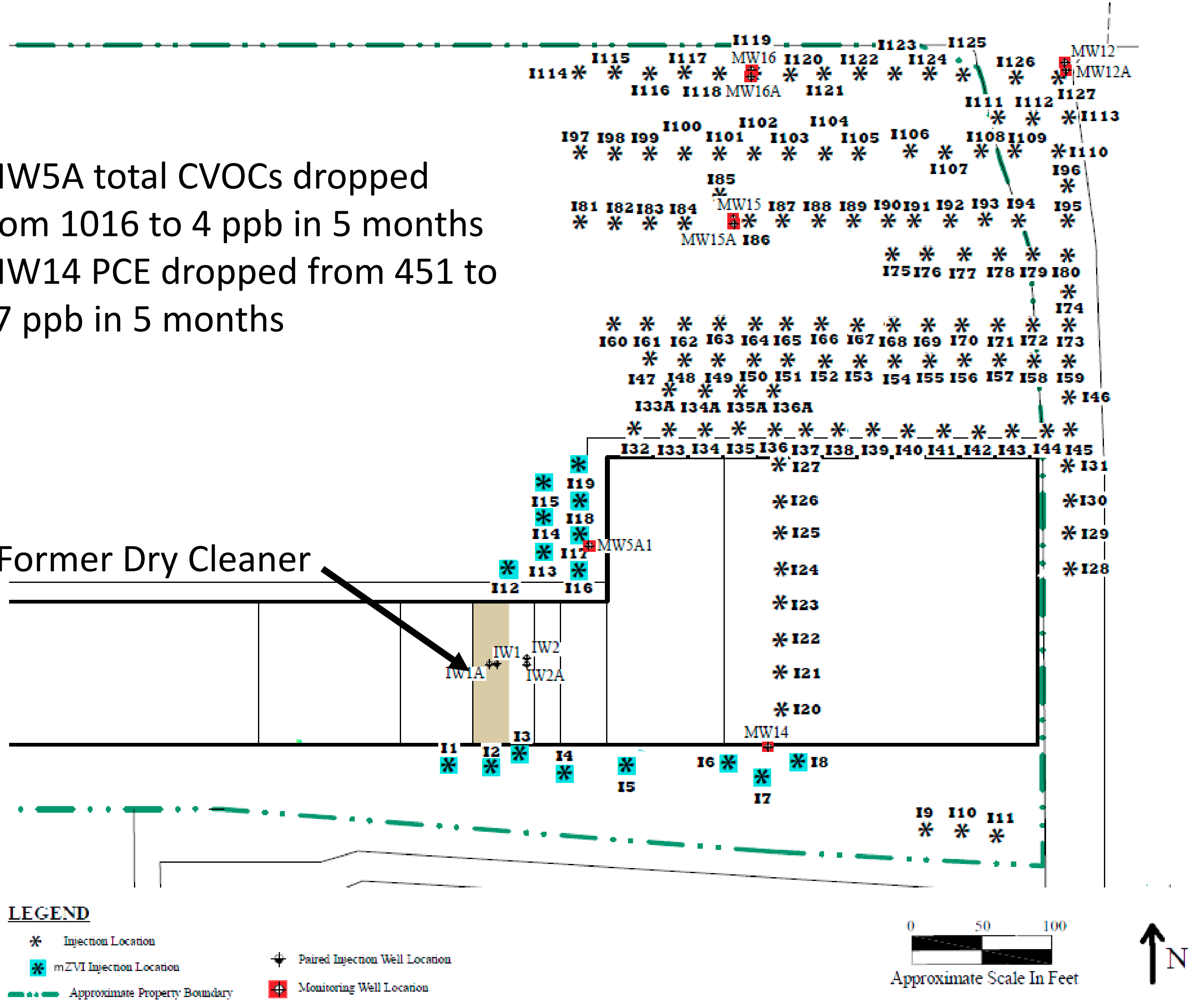


PCE Isoconcentration Contours



140 Injection Points

- MW5A total CVOCs dropped from 1016 to 4 ppb in 5 months
- MW14 PCE dropped from 451 to 97 ppb in 5 months



Field Mixing

TASK™ EVO Self-Emulsifier totes

Bulk tanker delivery of soybean oil

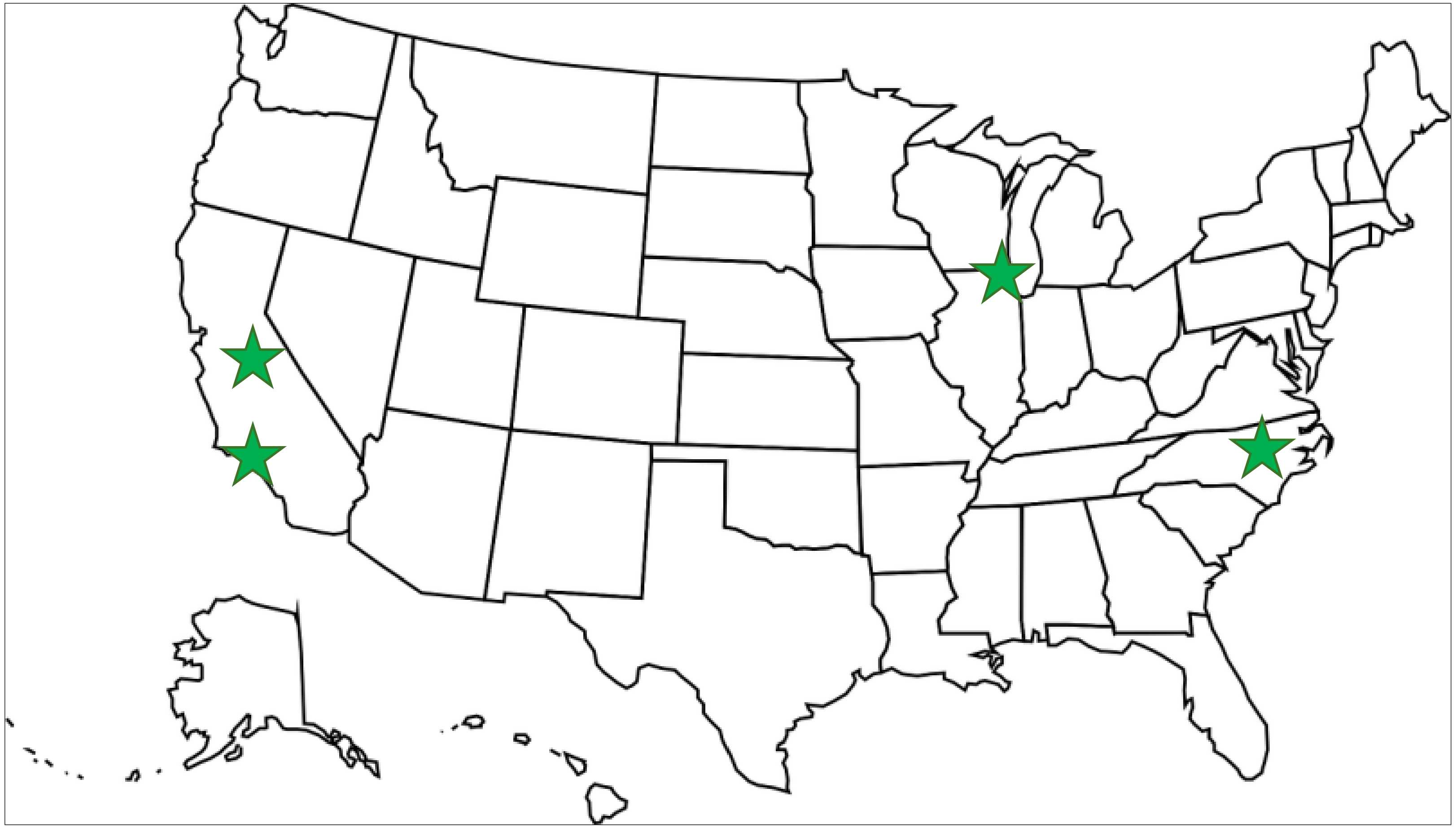
Quality Control Testing

Field prepared EDS-ER™

Add Water

Field prepared EVO

Distribution Centers



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Products and Services

ISCO

Modulated TersOx™ Liquid
Activated and Controlled Exothermic (ACE)

AEROBIC BIOREMEDIATION

TersOx™ Family of Products

ELECTRON ACCEPTORS FOR ANEROBIC BIOREMEDIATION

Sulfate Enhanced *In Situ* Remediation of Petroleum Hydrocarbons using *Nuristulfate®* and *NutriBind®*

ELECTRON DONORS

Enhanced Anerobic Bioremediation of Chlorinated Solvents

ZVI AND ISCR

ZVI Powders, mZVI, & ISR-Cl

NAPL REMEDIATION

Tersus Advanced Surface Kinetics (TASK™) liberates NAPL and captures them with enhanced recovery techniques

EQUIPMENT

Subsurface Delivery Systems
Additive injection and groundwater recirculation trailers available for short- or long-term leases

PERFORMANCE MONITORING

Compound Specific Isotope Analysis (CSIA) and Molecular Diagnostic Tools (MDT)

TECHNICAL SUPPORT

Professional technical services

Course Code ISNC

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