Strategies and Approaches for Employing Enhanced Reductive Dechlorination and *In Situ* Chemical Reduction at Challenging Sites

Dan Leigh P.G., CH.G.

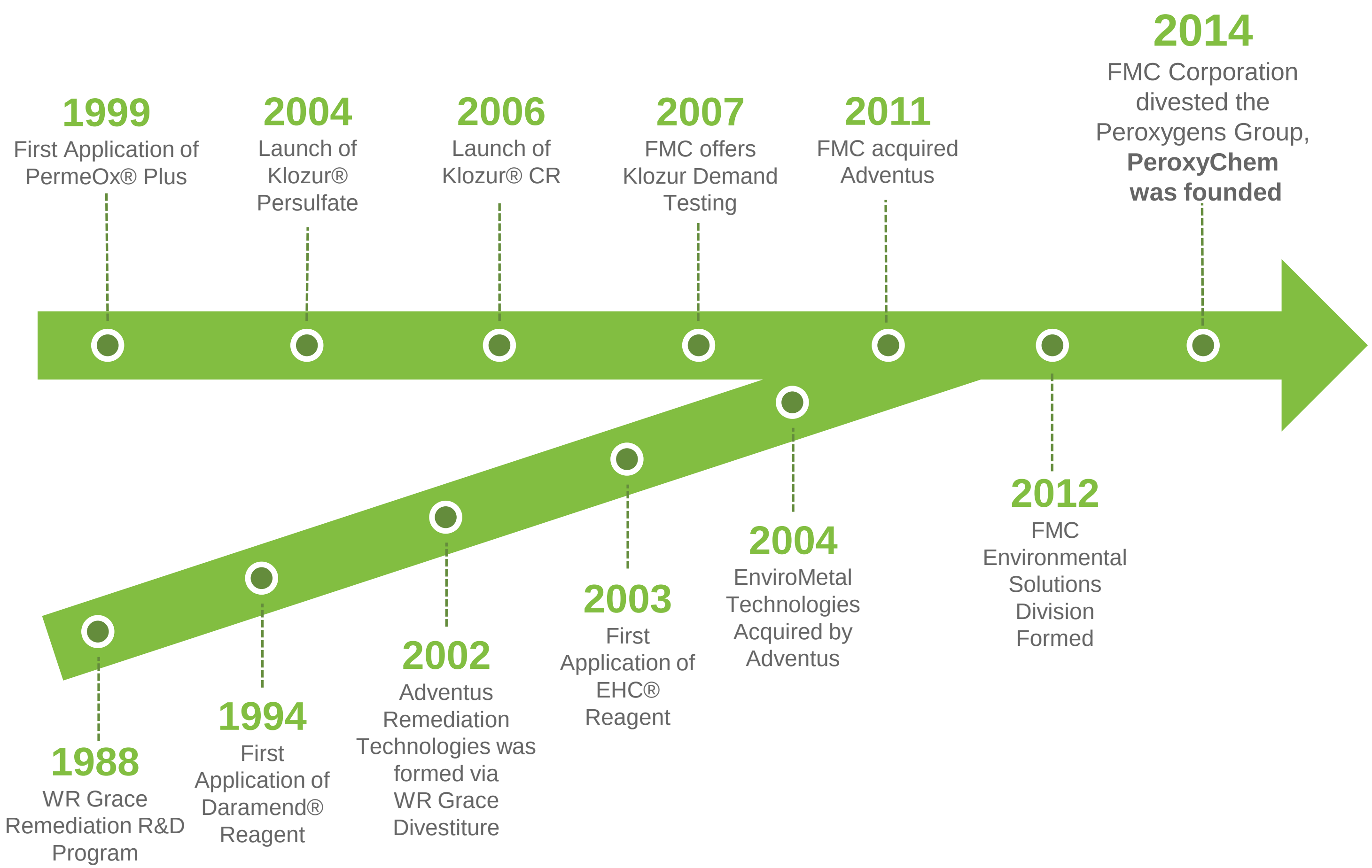
September 24, 2014

Environmental Solutions

Who We Were…

PeroxyChem

New Name.
Decades of Experience.



Who We Are…

PeroxyChem

Environmental Solutions

- Expert Technical Team
- Field Support
- Technical and Design Support
- Field-Proven, Diverse Technologies
- R&D and Treatability Laboratories
- Mixing and Handling Equipment

Field-Proven Portfolio of Remediation Technologies Based on Sound Science

***In Situ* Chemical Oxidation**

1. Klozur® persulfate
2. Klozur® CR

In Situ Chemical Reduction

3. EHC®
4. EHC® Liquid
5. Daramend®

Aerobic Bioremediation

6. Terramend®
7. PermeOx® Ultra

Immobilization/Stabilization

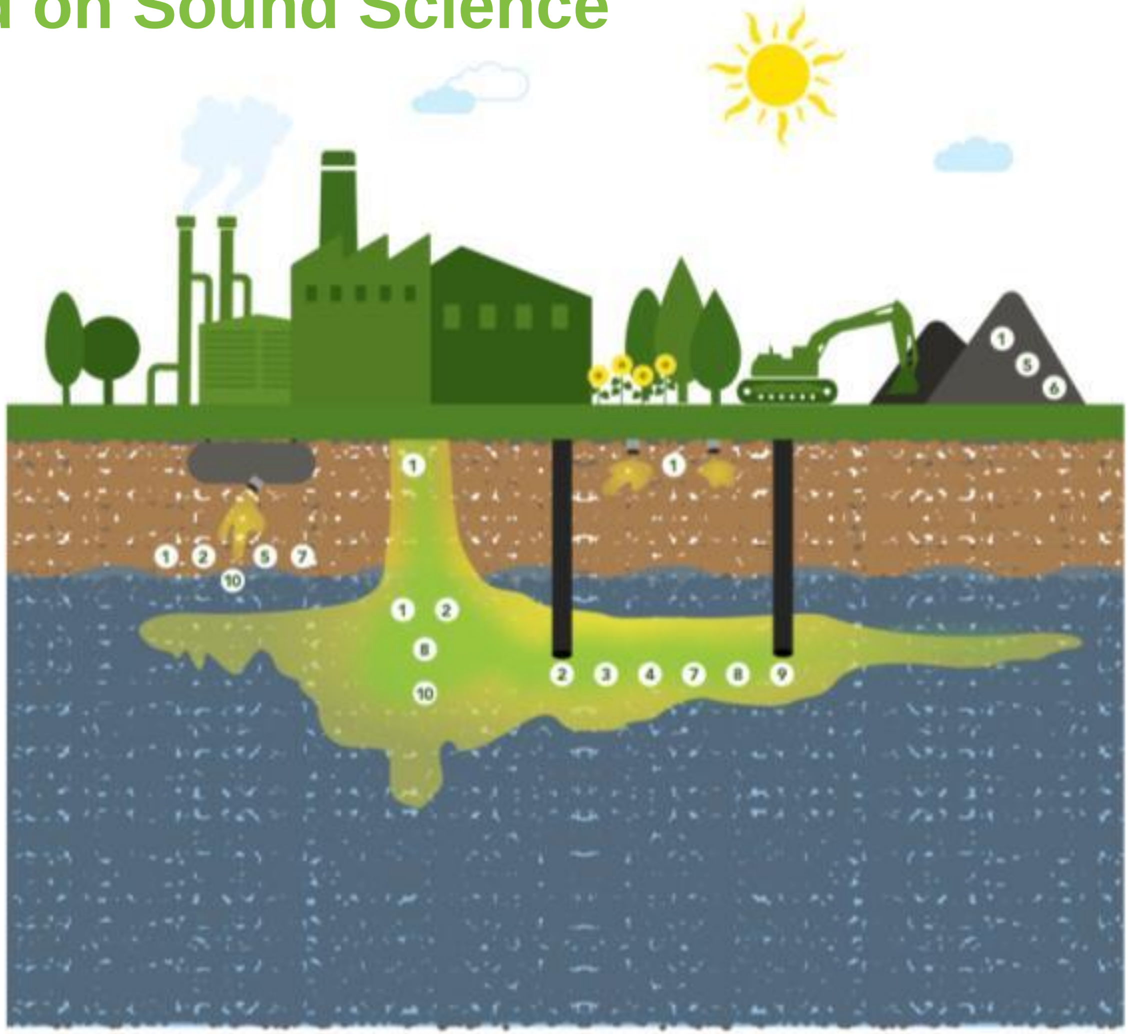
8. EHC® Metals and MetaFix™

Enhanced Reductive Dechlorination

9. ELS™

NAPL Stabilization/Mass Flux Reduction

10. ISGS™



In Situ Chemical Reduction

Purpose of this presentation:

- **Present Biological and In Situ Chemical Reduction Processes**
- **Present field comparison of Biotic approach (ERD) to ISCR Approach**
- **Demonstrate how ISCR enhances biological processes in high sulfate aquifers.**

ISCR is defined as "a process that combines biotic and abiotic reactions to treat contaminants while creating reducing conditions"

Process	Amendments
Enhanced Reductive Dechlorination (Biotic Only)	Organic carbon substrates (eg: mulch , cheese whey, vegetable oil, ELS etc…) + Bacteria
In Situ Chemical Reduction	Organic carbon substrates + ZVI (eg: EHC®, EHC®-Liquid, ELS + ZVI etc..) +/- Bacteria

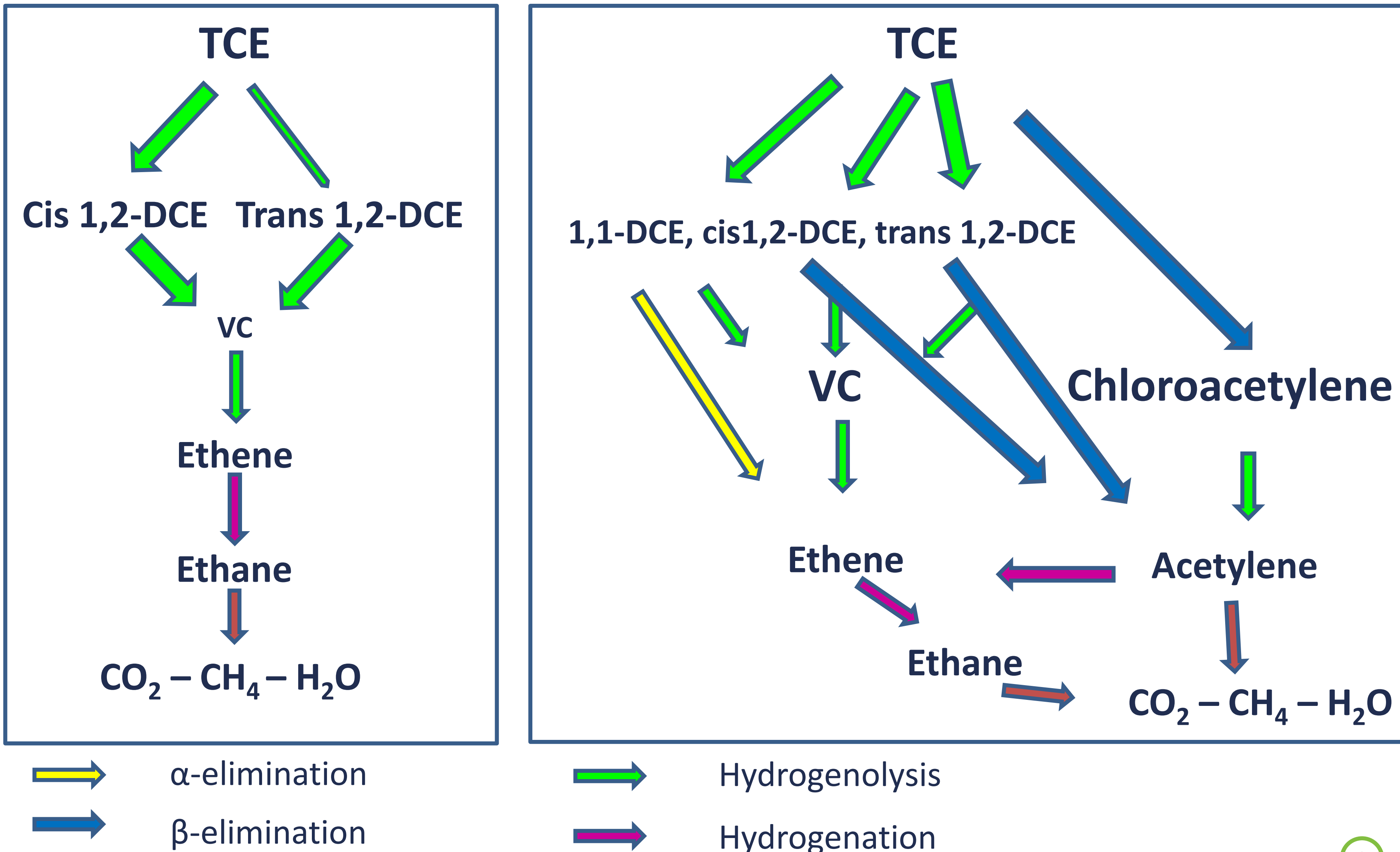
ISCR Reaction Pathways

Environmental Solutions

PeroxyChem

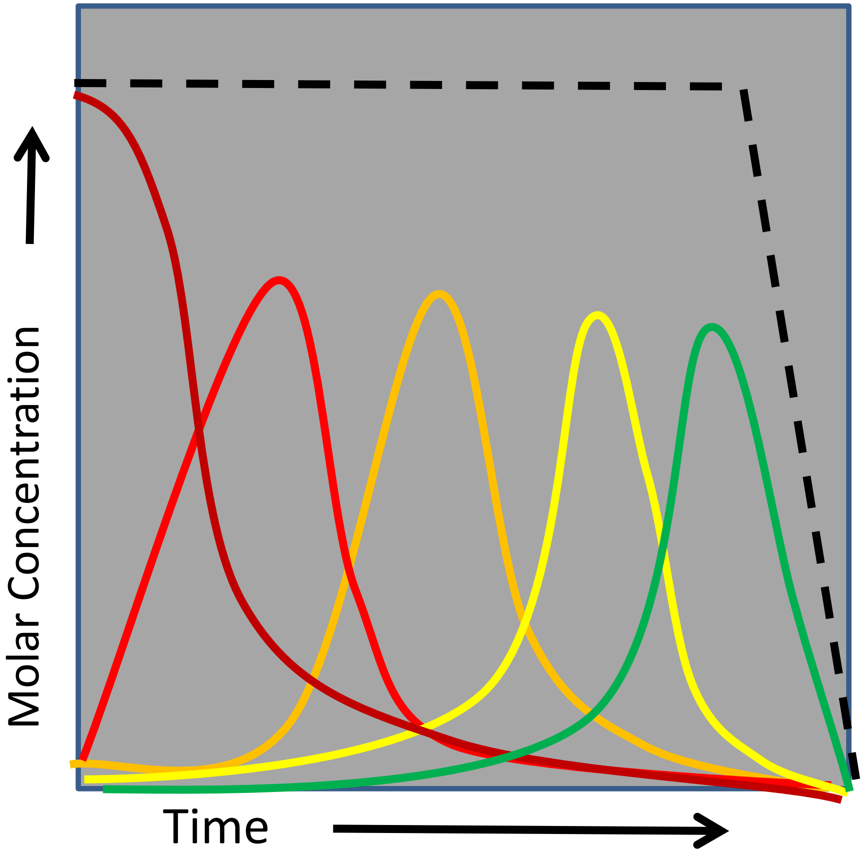
Biotic

Abiotic

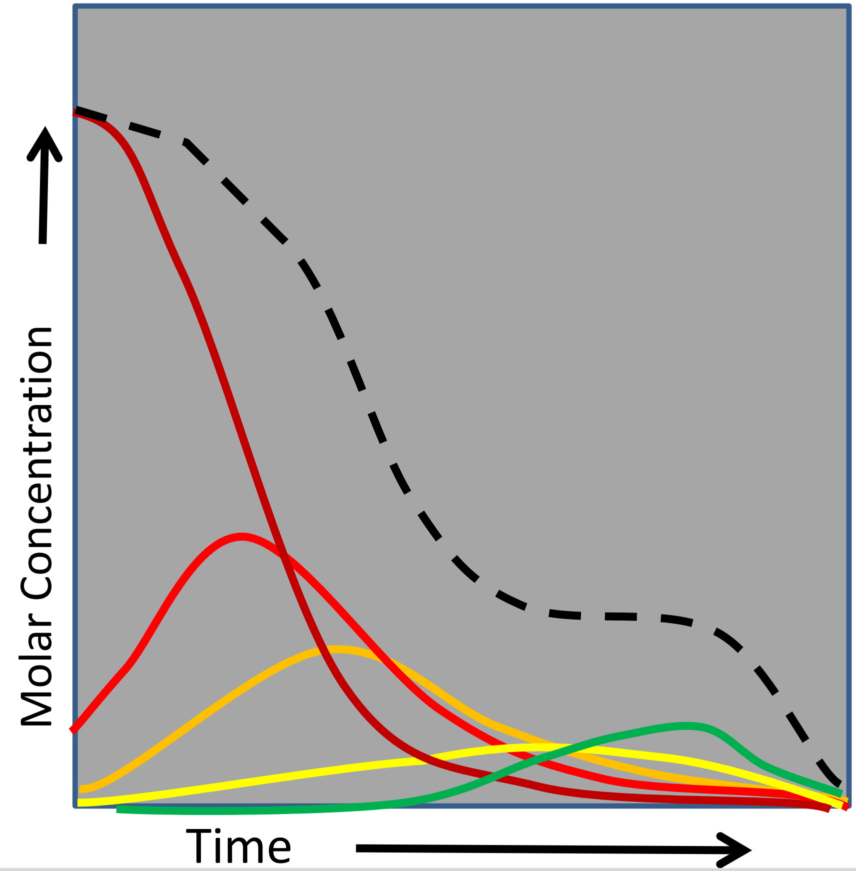


Anticipated Change in CE Molar Concentration

Biological Degradation (Reductive Dechlorination)



Abiotic Degradation



PCE TCE DCE VC Ethene

Total Molar Concentration

Environmental Solutions

Case Study 1

PeroxyChem

- **TCE plume is >700 feet long and extends up to 95 feet bgs**
- **Aquifer consists of interbedded silts, sands and clays.**
- **Max TCE concentration about 6 mg/L. Very little 1,2-DCE. No VC**
- **Aquifer is highly aerobic (~ 4 to 7 mg/L DO)**
- **Dhc not present**

Pay for Performance

Navy wanted most aggressive approach possible to achieve the remedial goals in the shortest amount of time.

- Navy used Performance Based Contract.
- Payment based on achieving remedial goals within specified time.

Navy's /CB&I selected approach - ISCR:

- **Maximize substrate longevity and distribution using Emulsified Lecithin Substrate**
- **Enhance biotic degradation with abiotic processes using Zero Valent Iron**
- **Apply VC respiring culture (SDC-9™) to treat residual VC.**
- **Maximize distribution by fracturing and high pressure / flow substrate injection**

What is ELS™ Emulsified Lecithin Substrate?

Composition:

- **Food-grade lecithin,**

- **Natural occurring substance**

- **Mixture of choline, fatty acids, glycerol, glycolipids, triglycerides, & phospholipids , and can also contain sugars.**

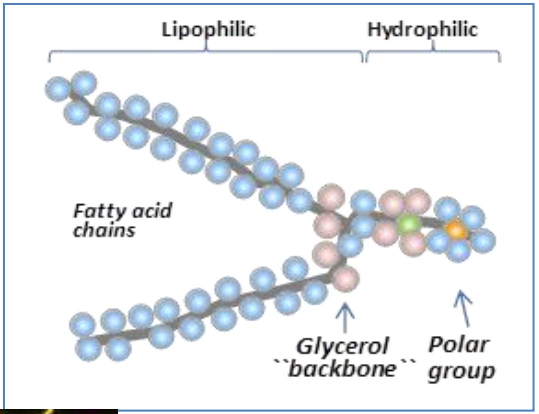
- **Polysaccharides and sugars to support rapid creation of reducing conditions**

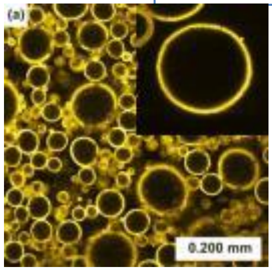
- **Phospholipids for long-term release of organic carbohydrate**

•Easy to use:
  •Stable emulsion

Why Select ELS?

- **Slow release nutrients:**
- **Provides both organic nitrogen and phosphorus**
  - **Long lasting:**
    - **Extended release profile of 1 to 3 years**
- **Good distribution:**
  - **Hydrophilic for enhanced distribution**
  - **Small droplet size (60% <1µm and 85% <2µm)**
- **Efficient source of hydrogen:**
  - **High yield of H_2 produced/gram substrate**





Product	Product Concentration (%)	Theoretical Hydrogen yield * (g H_2/g substrate, estimate, as delivered)
ELS™ Concentrate	100	0.324
Emulsified Vegetable Oil	100	0.359
HRC®	100	0.141
Sodium Lactate Solution	100	0.075

Abiotic Processes

ZVI added to:

- Maintain pH in range favorable for ERD
- Bypass generation of toxic daughter products
- Reduction of daughter products more rapidly achieves goals
- Provide long term process for continued dechlorination.

Concord Naval Weapons Station IR Site 29

Pilot Test Comparison

Two Pilot Tests Conducted

Biotic Only – (2011 – 2012)

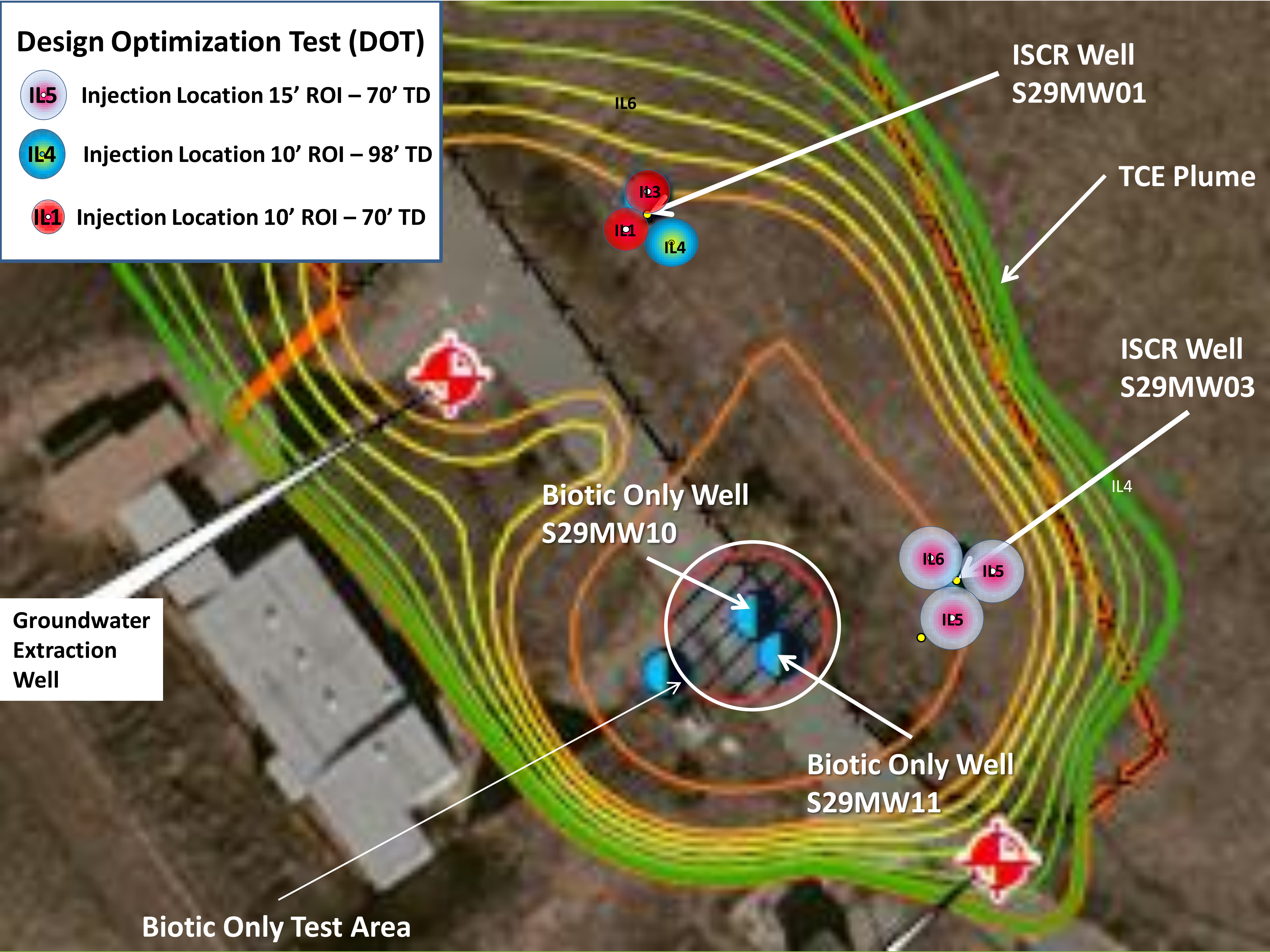
In Situ Chemical Reduction (ISCR) – (2013 – 2014)

Biotic Only (ERD) Approach:

- Direct push, high pressure injection – 6 foot radius
- Injection water preconditioned with sodium lactate
- Emulsified vegetable oil ~6 grams/Liter, (buffered)
- Bioaugmentation (SDC-9™)
- H_2 added to one well (S29MW10)

In Situ Chemical Reduction (ISCR) Approach:

- Direct push, fracking and high pressure injection - 10 ' & 15 feet Radius
- Injection water preconditioned with sodium lactate
- Emulsified Lecithin Substrate (ELS) ~2 grams/Liter
- Bioaugmentation (SDC-9™)
- Zero Valent Iron (ZVI) suspended in guar



Design Optimization Test (DOT)
IL5
Injection Location 15' ROI – 70' TD
IL4
Injection Location 10' ROI – 98' TD
IL1
Injection Location 10' ROI – 70' TD
IL6
IL3
IL1
IL4
ISCR Well
S29MW01
TCE Plume
ISCR Well
S29MW03
IL4
Biotic Only Well
S29MW10
IL6
IL5
IL5
Groundwater
Extraction
Well
Biotic Only Well
S29MW11
Biotic Only Test Area

Environmental Solutions

ELS Concentrate

PeroxyChem

Environmental Solutions

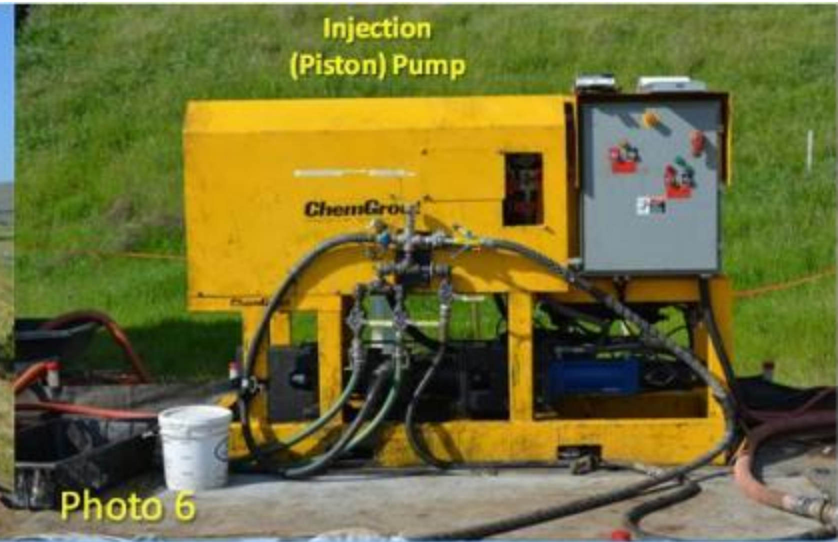
ELS 25% Emulsion

PeroxyChem

Treatment Equipment

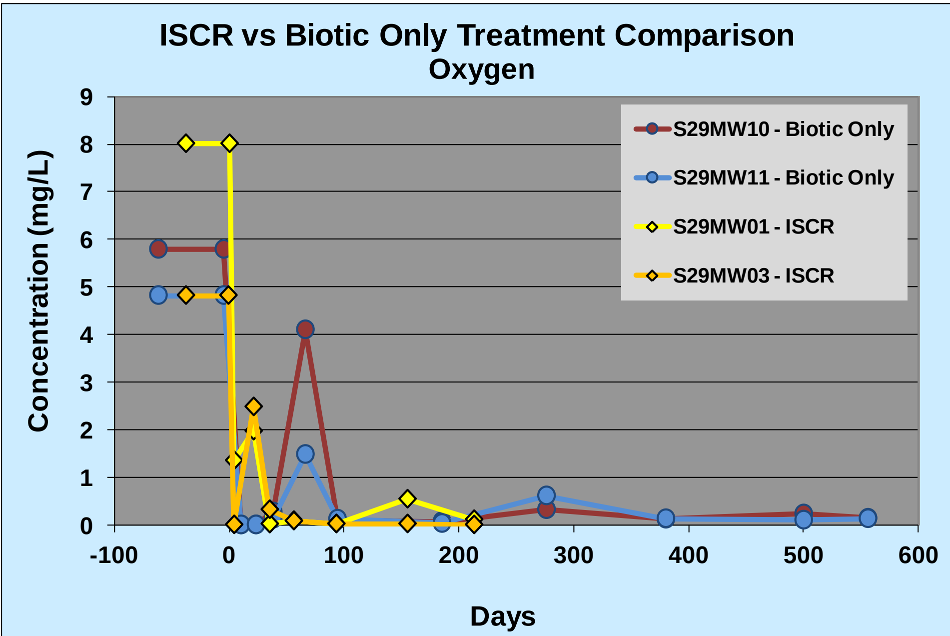
Treatment Equipment

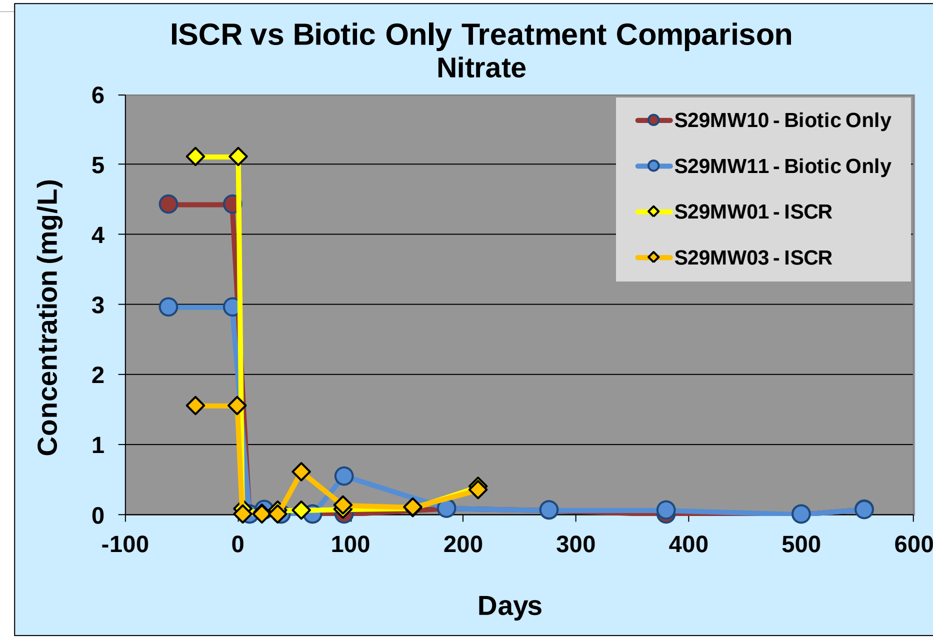
Treatment Equipment

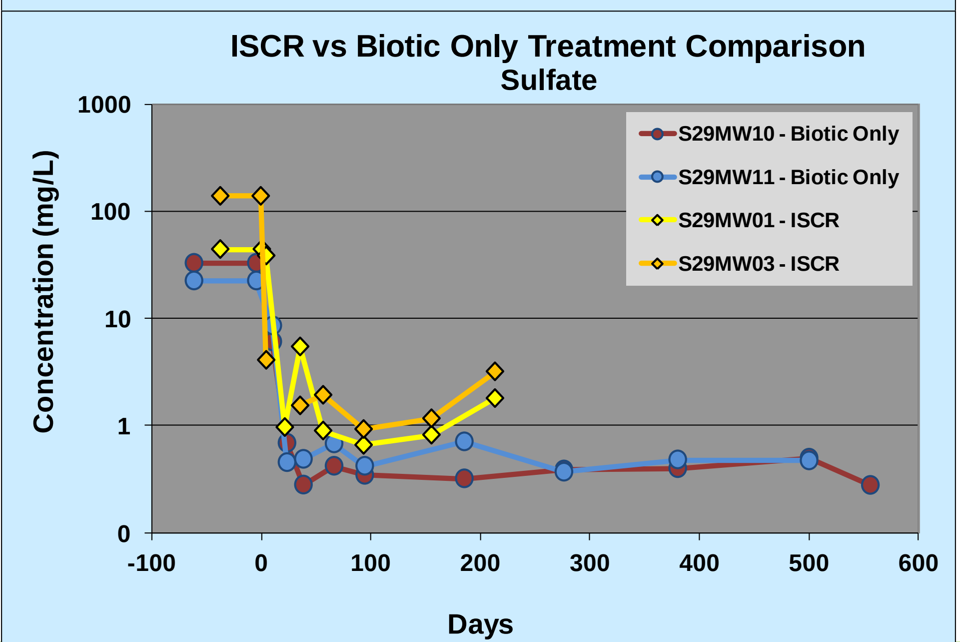


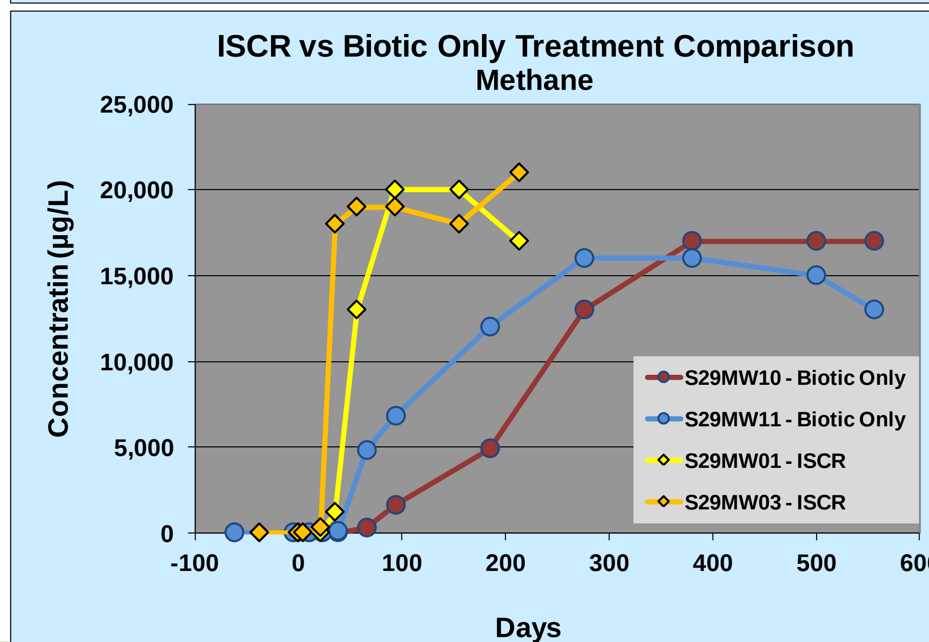
How Far is Substrate Distributed?

Analytical Results

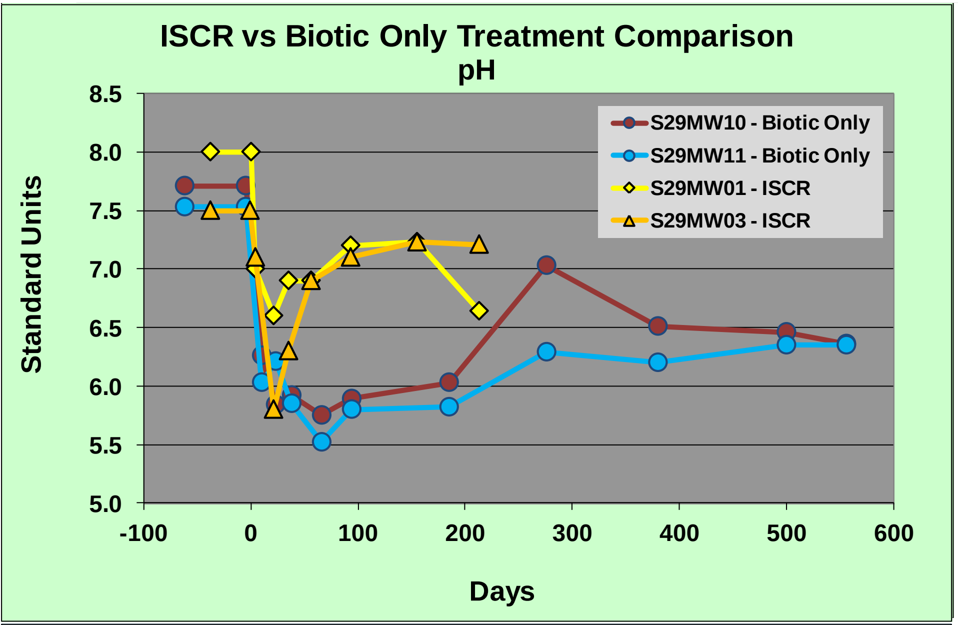


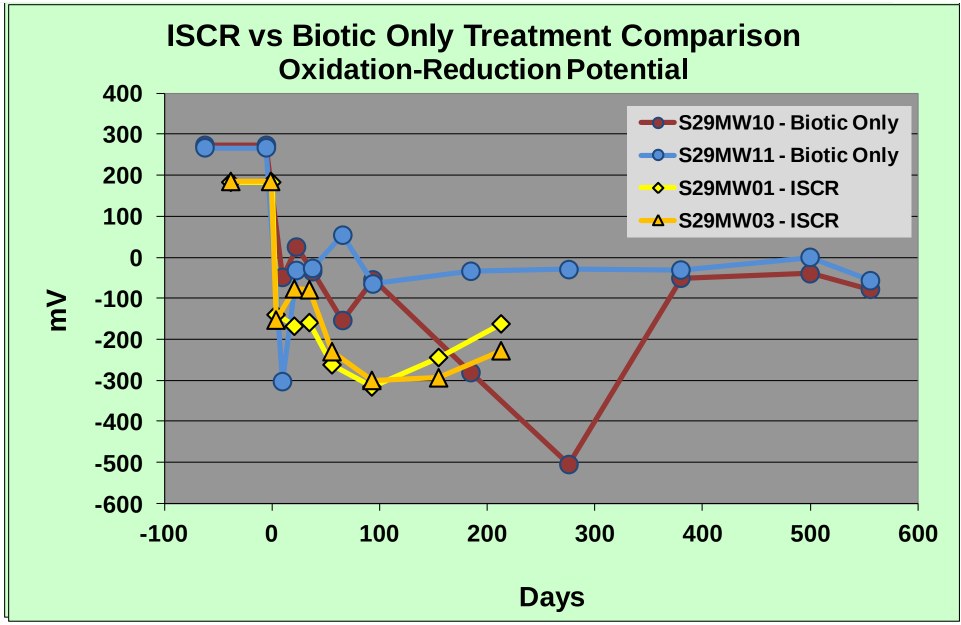


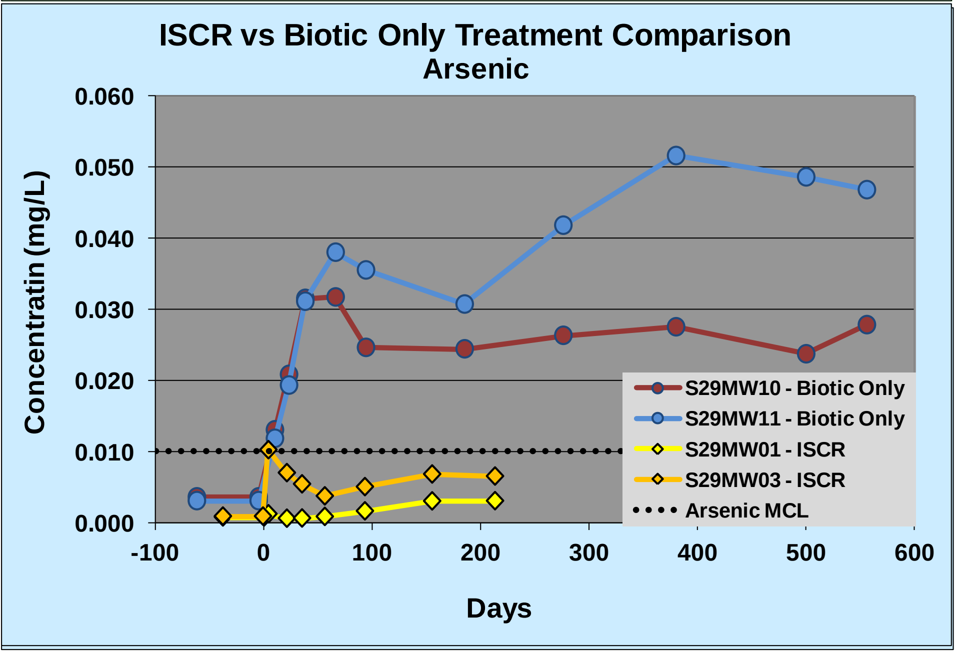


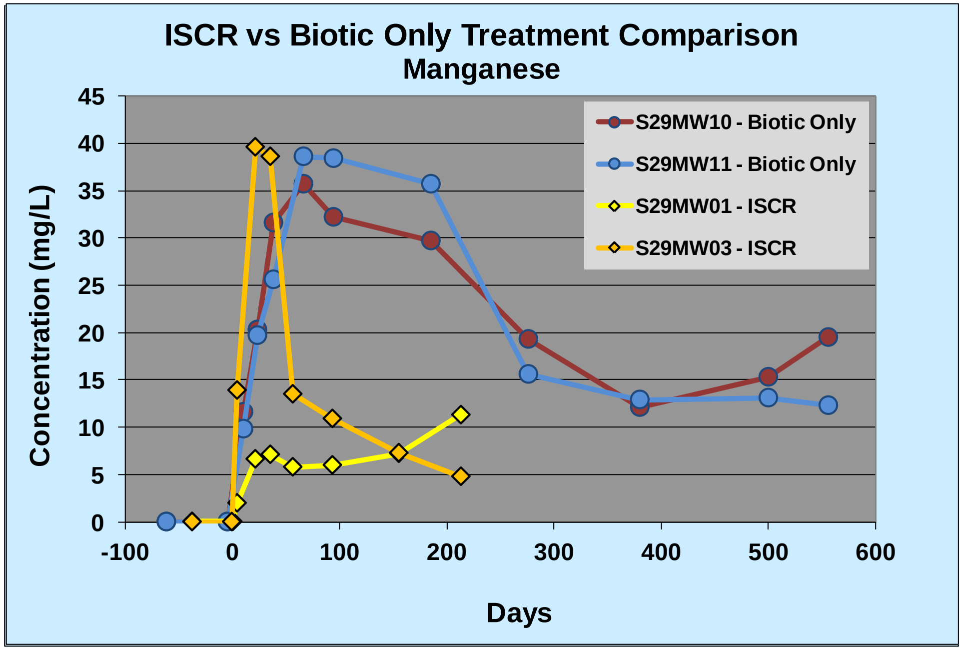


Analytical Results

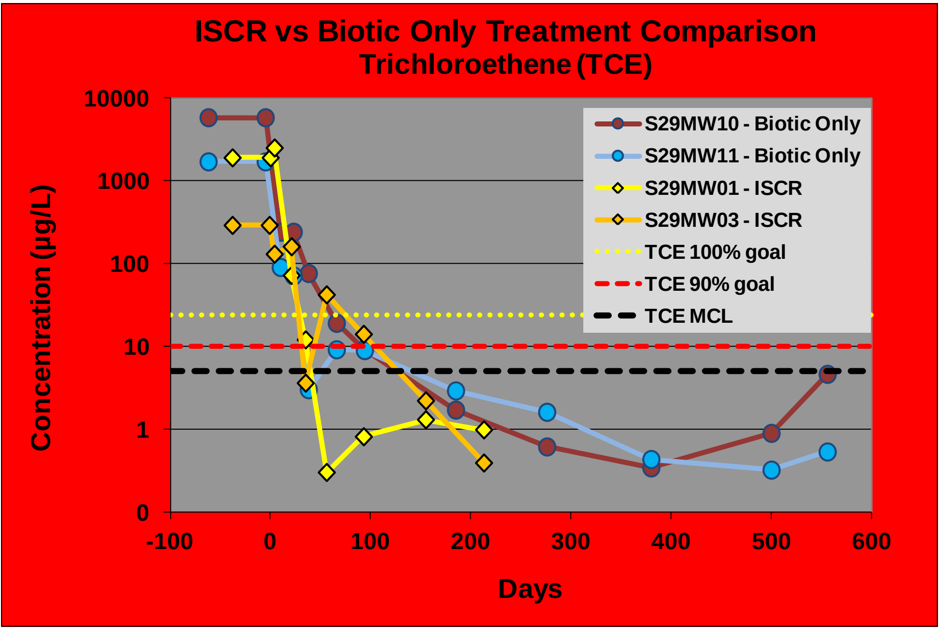


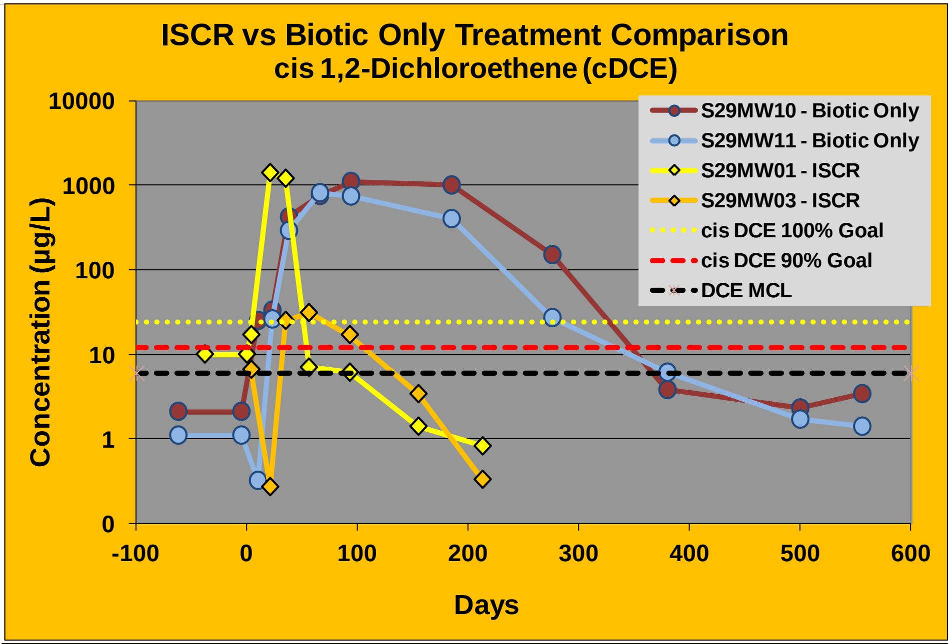


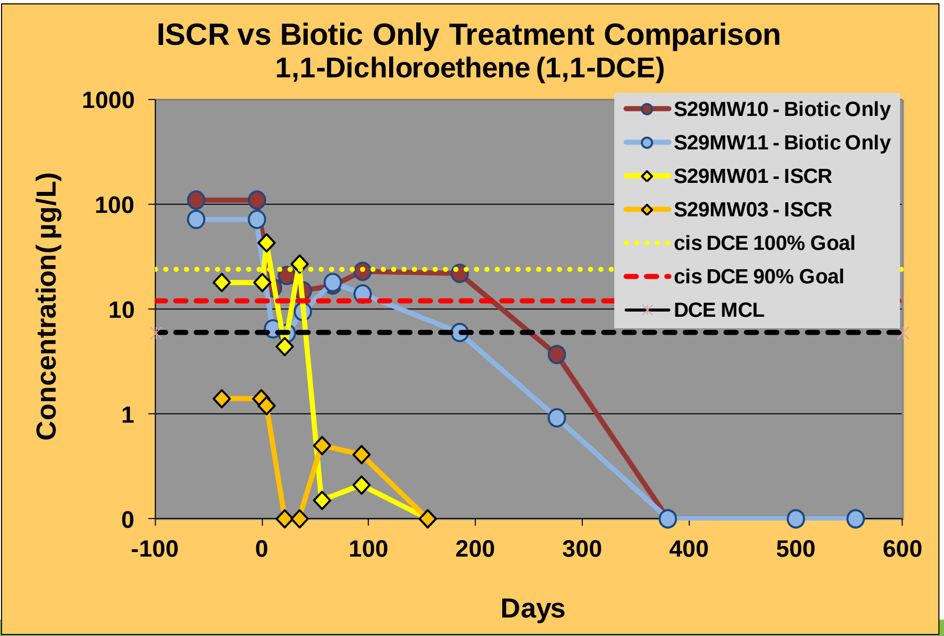


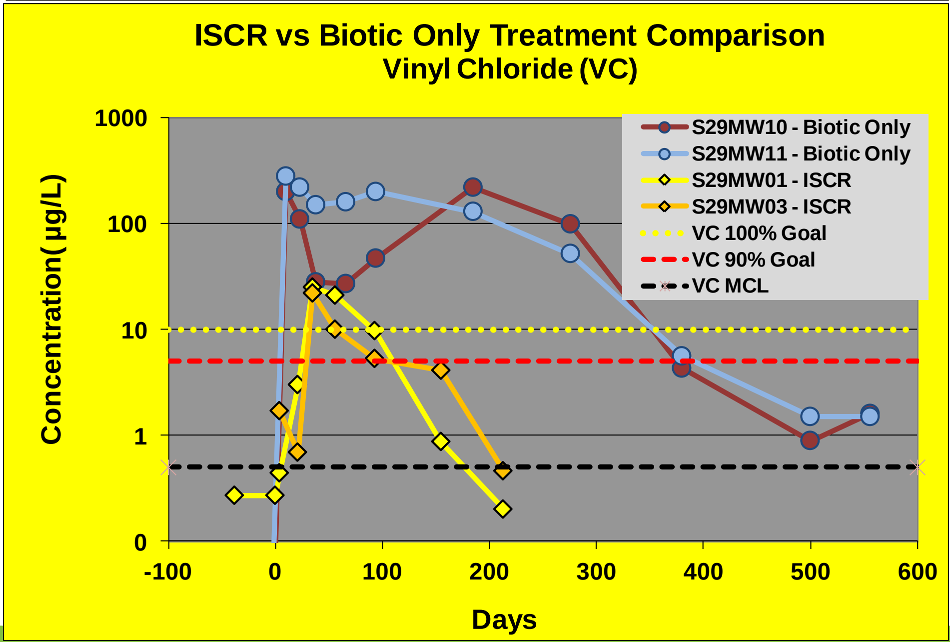


Analytical Results





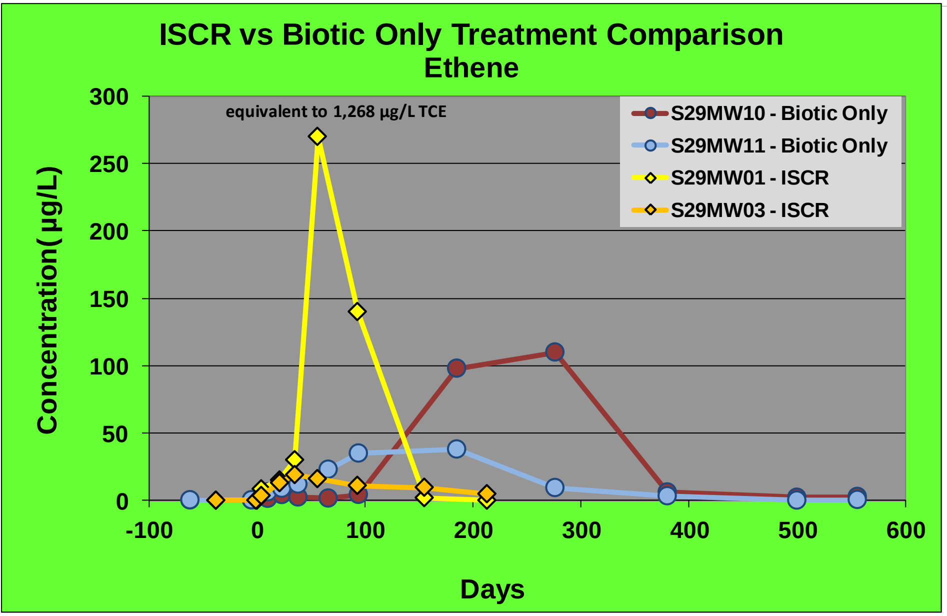


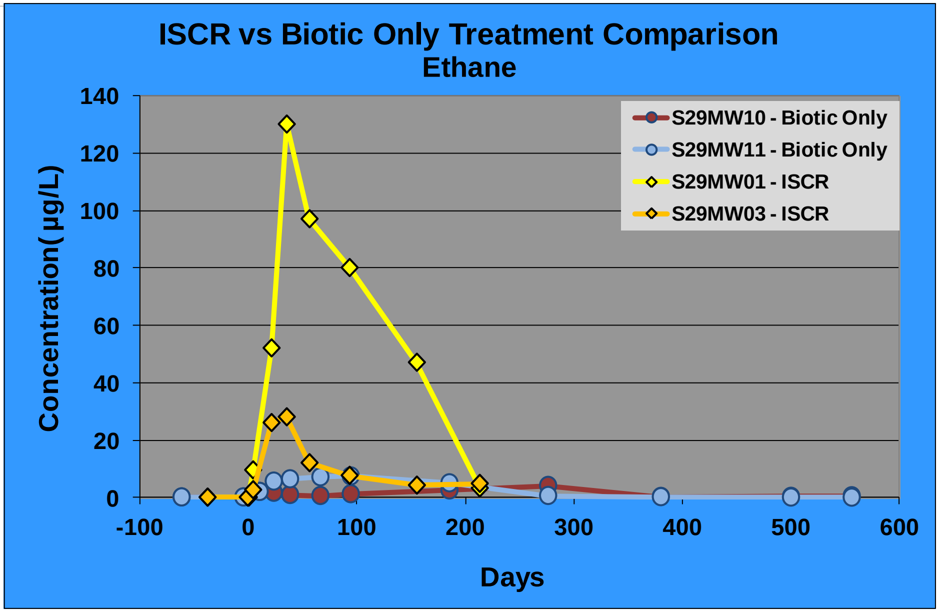


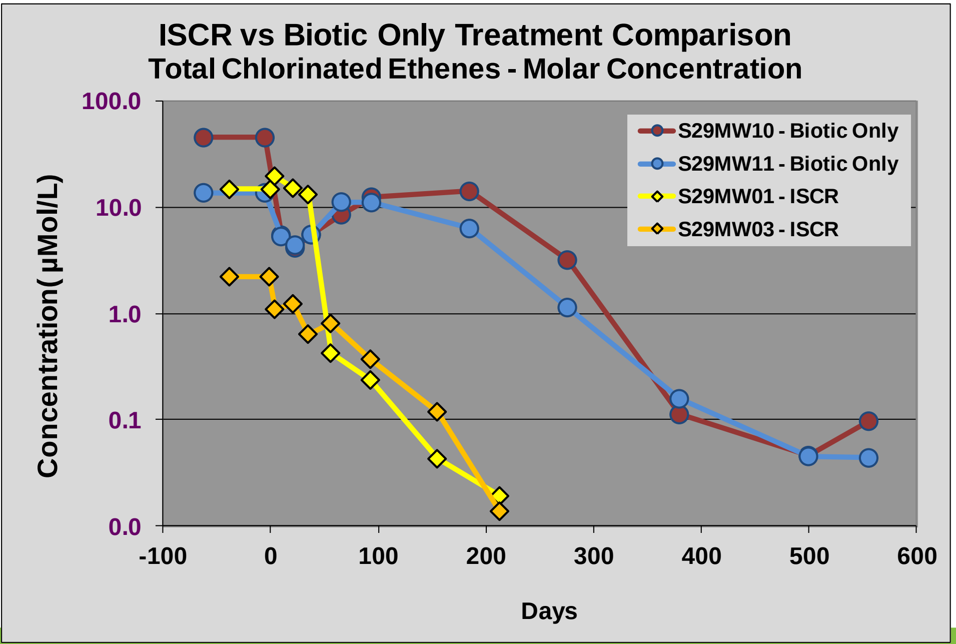
Analytical Results

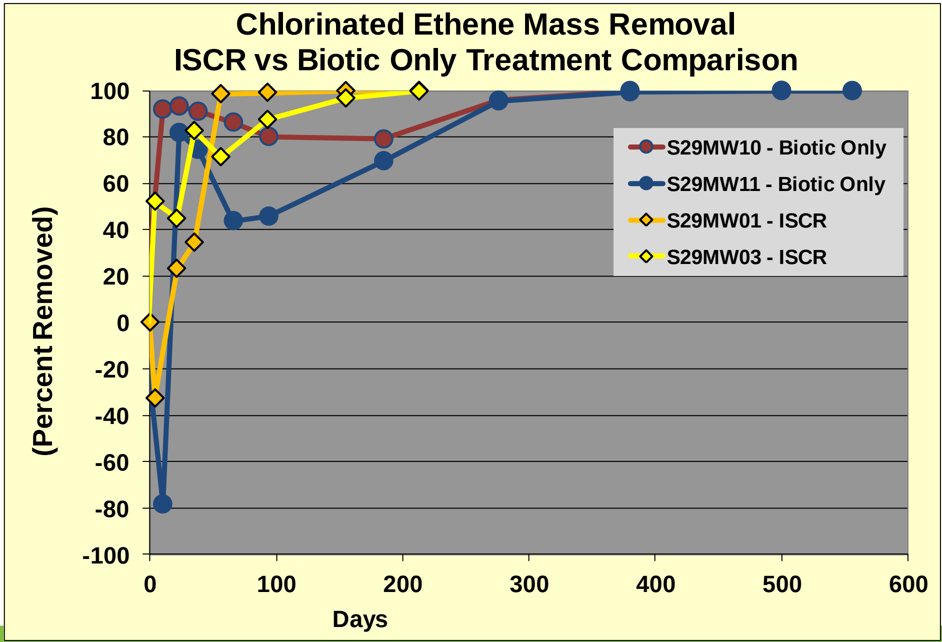
Environmental Solutions

PeroxyChem

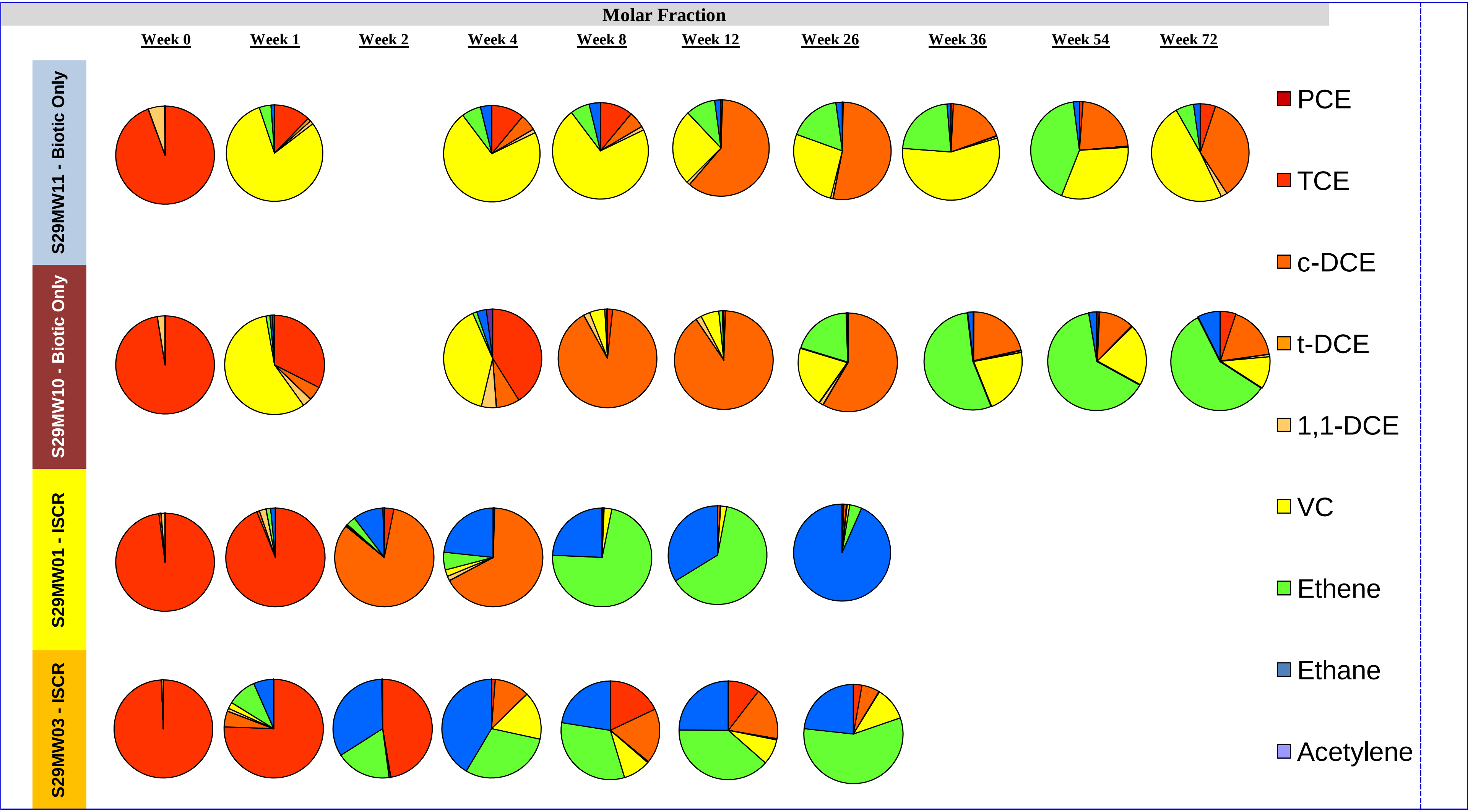








Pilot Test Analytical Results



Bio/ISCR Comparison Summary

- ELS is a highly effective substrate for ERD
- ISCR minimized dissolved arsenic and manganese
- ISCR more aggressive than ERD only approach
- DCE degradation primarily abiotic – does not generate VC
- Rapid remediation time attributable to abiotic degradation of DCE
- Navy's goals achieved in 1/3 time using ISCR vs. ERD only approach
- ISCR process has been applied to entire plume

High Sulfate Aquifer

Site Conditions

- Elevated PCE >2000 µg/L
- Aerobic Aquifer (DO ~5.0 mg/L)
- Sulfate up to 3,000 mg/L
- Previous bio only pilot tests unsuccessful
- Incomplete degradation of PCE
- Potential sulfide inhibition
- Enhanced Reductive Dechlorination considered not applicable

Our Objective

Determine if In Situ Chemical Reduction (ISCR) is capable of Treating PCE in aerobic, high sulfate aquifer

Determine if of soluble ferrous iron in EHC®-Liquid can enhances precipitation of iron sulfide.

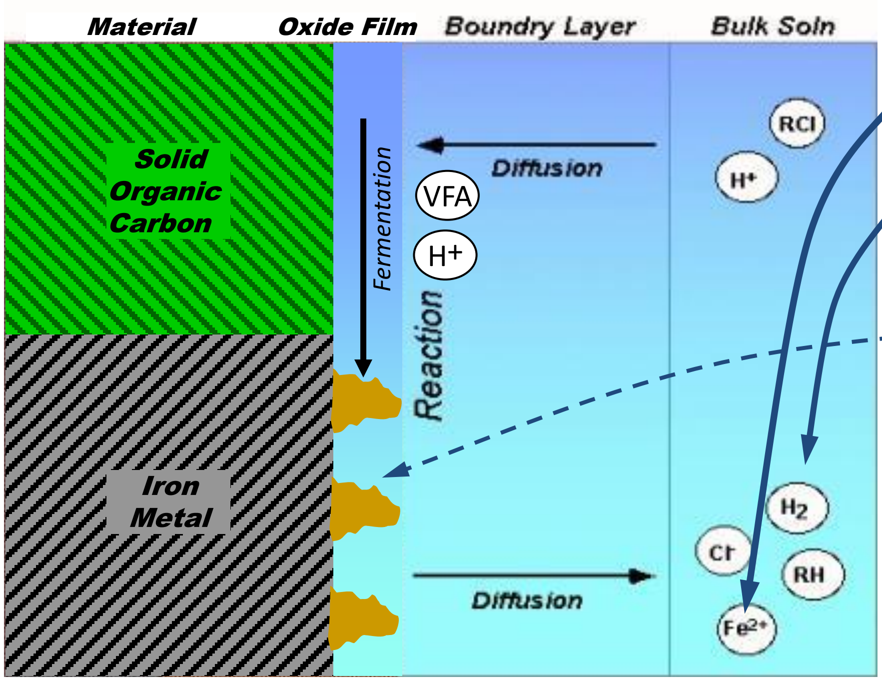
Does removal of sulfate/sulfide result in dechlorination of PCE?

Approach:

Conduct bench test to evaluate two ISCR products

- **EHC®**
- **EHC®Liquid + Soluble Fe^{2+}**

EHC - Carbon Fermentation + ZVI Corrosion: Multiple Dechlorination Mechanisms



Fe^{2+} generation

H_2 generation

ZVI Reactions:

$Fe^0 \rightarrow \mathbf{Fe^{2+}} + 2e^-$

$2H_2O \rightarrow 2H^+ + 2OH^-$

$2H^+ + 2e^- \rightarrow H_{2(g)}$

$R\text{-}Cl + H^+ + 2e^- \rightarrow R\text{-}H + Cl^-$

Production of organic acids (VFAs):

- Serves as electron donor for microbial reduction of CVOCs and other oxidized species such as O_2, NO_3,
- **Sulfate SO_4 is reduced to sulfide (S^-)**
- **Fe^{2+} Combines with S^- to precipitate FeS**
- The release of acids keeps the pH down and thereby serve to reduce precipitate formation on ZVI surfaces to increase reactivity
- Increase rate of iron corrosion/H_2 generation

Favorable thermodynamic conditions for dechlorination:

- Combined oxygen consumption from carbon fermentation and iron oxidation → Strongly reduced environment (-250 to -500 mV)
- High electron/H^+ pressure

EHC-Liquid: Reaction Chemistry

Like EHC, EHC-L supports degradation of organic constituents by enhancing:

- anaerobic bioremediation processes
- abiotic reduction reactions

❖ As bacteria feed on the soluble carbon, they consume dissolved oxygen and other electron acceptors, thereby reducing the redox potential in groundwater.

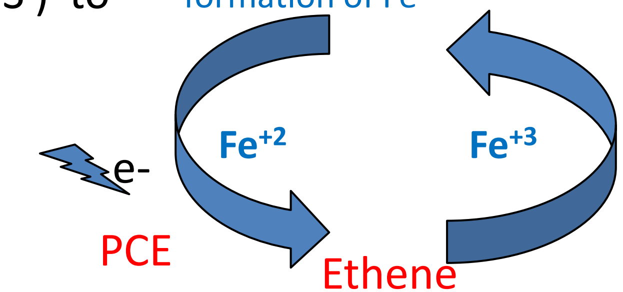
❖ Iron reducing microbes will continuously regenerate ferrous minerals and a cycle is established.

❖ The soluble carbon provides molecular hydrogen (H_2) for biologically mediated enhanced reductive dechlorination (ERD)

❖ The soluble ferrous iron (Fe^{2+}) combines with sulfide (S^-) to generate reactive iron sulfide (FeS) species in situ

❖ Ferrous iron may also control dissolved phase heavy metals by promoting formation of insoluble forms (e.g., arsenopyrite from arsenic).

ISCR reactions of Fe^{+2} with contaminants and formation of Fe^{+3}



Bacterial extraction of electrons from carbon restores Ferric (Fe^{+3}) to Ferrous (Fe^{+2})

Environmental Solutions

Biogeochemical Transformation

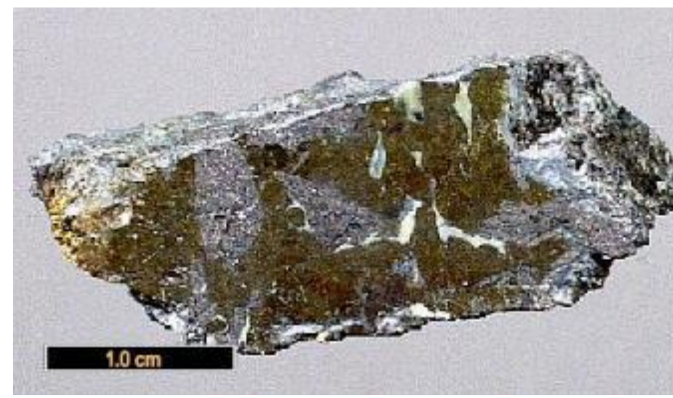
PeroxyChem

Processes where contaminants are degraded by abiotic reactions with naturally occurring and biogenically-formed minerals in the subsurface.

Reactive minerals include iron sulfides (e.g. pyrite, mackinawite, greigite) and oxides (e.g. magnetite)

Pyrite (FeS_2)

Magnetite(Fe_3O_4)



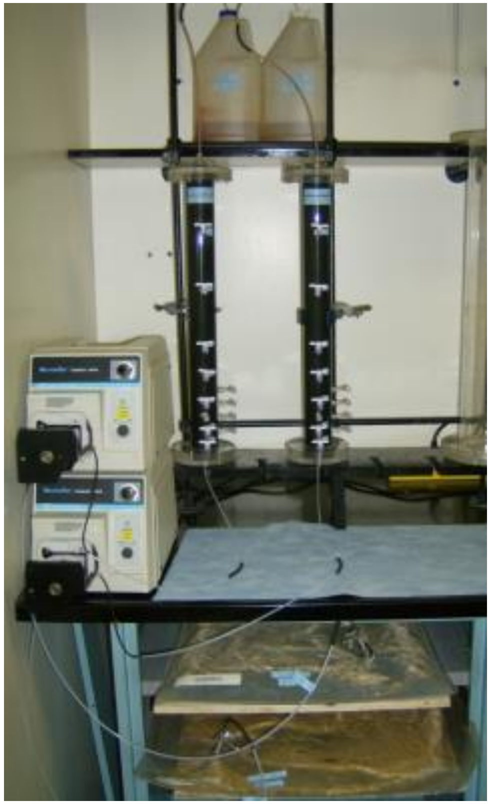
Mackinawite ($Fe_{(1+x)}S$

ß–Elimination does not generate stable toxic daughter products

Microcosm Setup

Bench Test Conducted at PeroxyChem's laboratory Mississauga, ON

Sediment and groundwater samples collected from source area wells



Some sediment in each of the microcosms

PCE – 170 µg/L Spiked to 1,800 µg/L

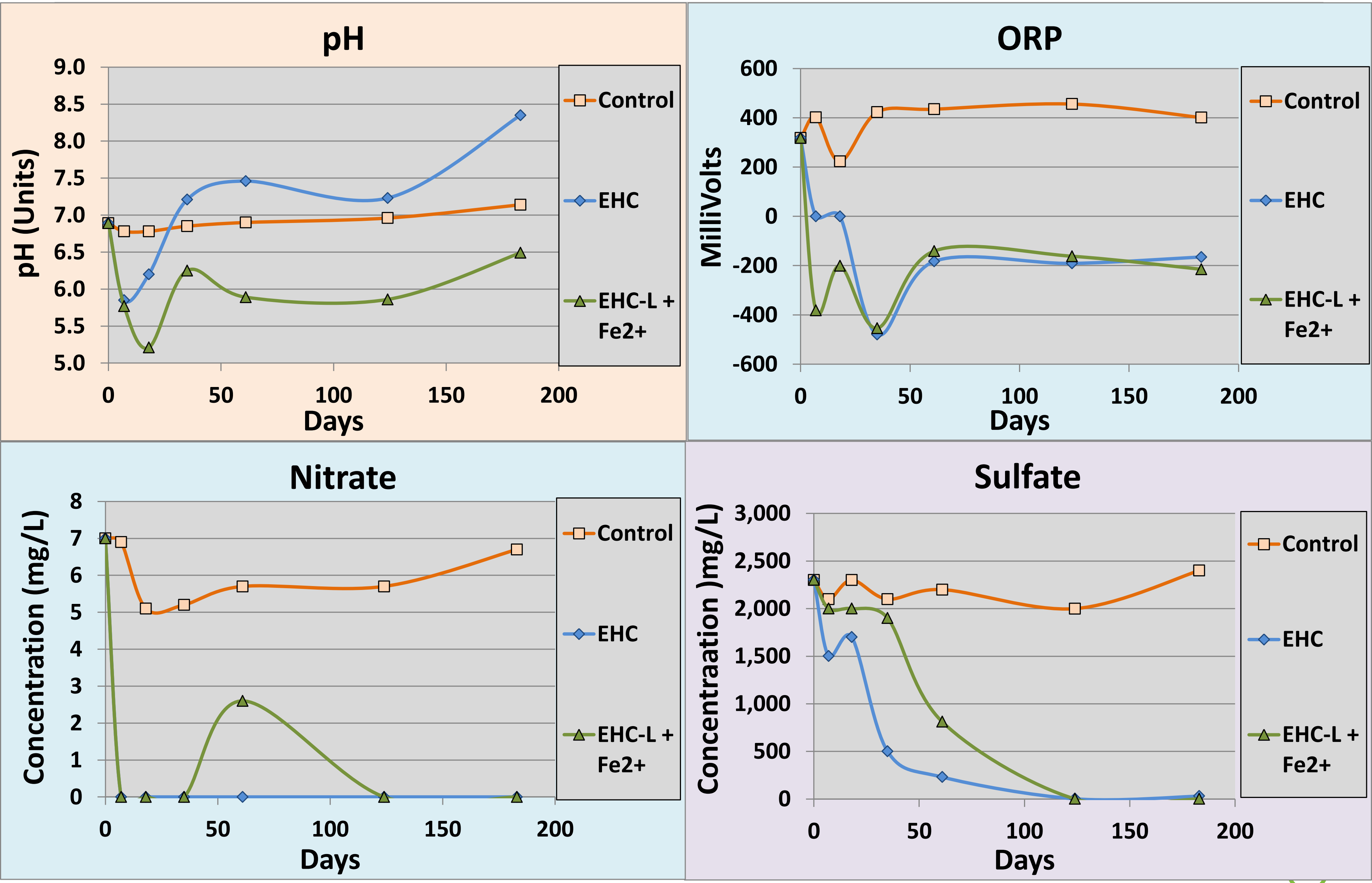
Sulfate – 1,800 mg/L Spiked to 2,300 mg/L

SDC-9^{TM} Dhc ~ 1X10^{8} cells/L

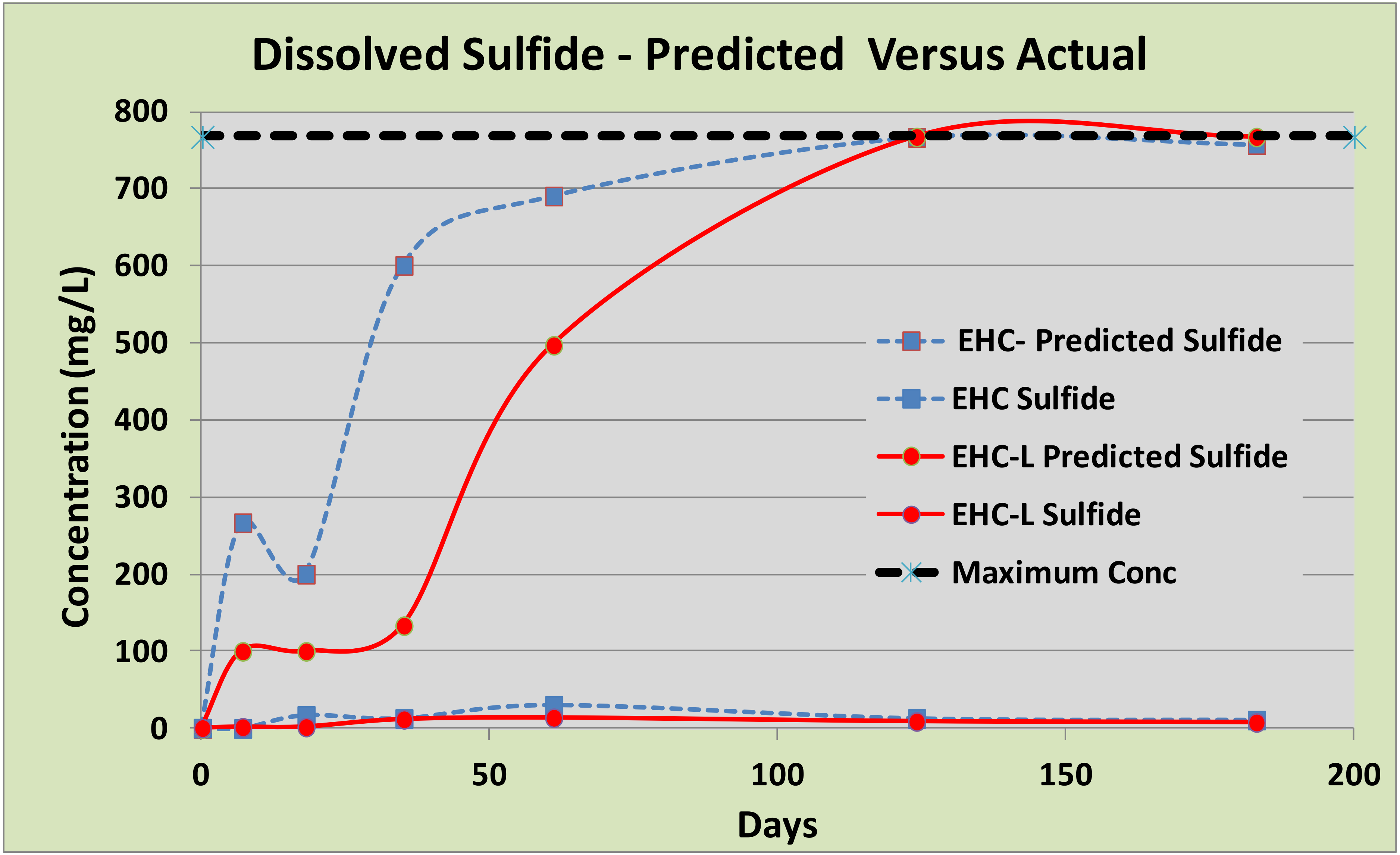
EHC-Liquid 10 g/L + additional 14 g/L soluble iron

EHC – 10 g/L

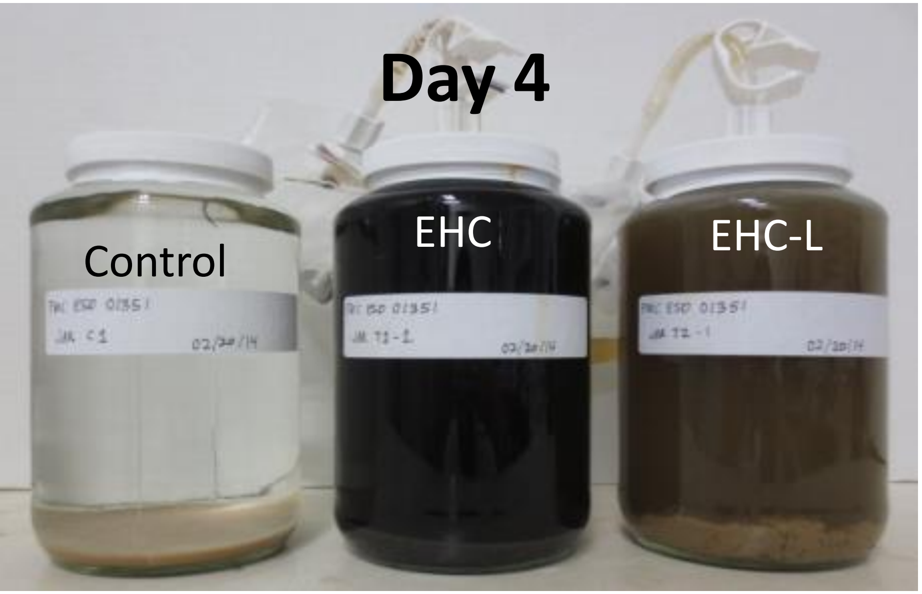
Analytical Results

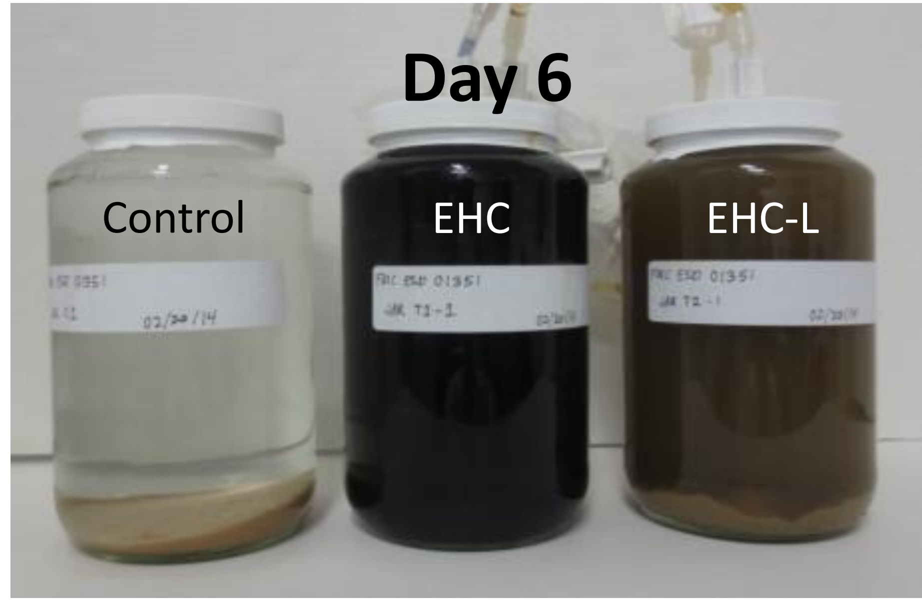


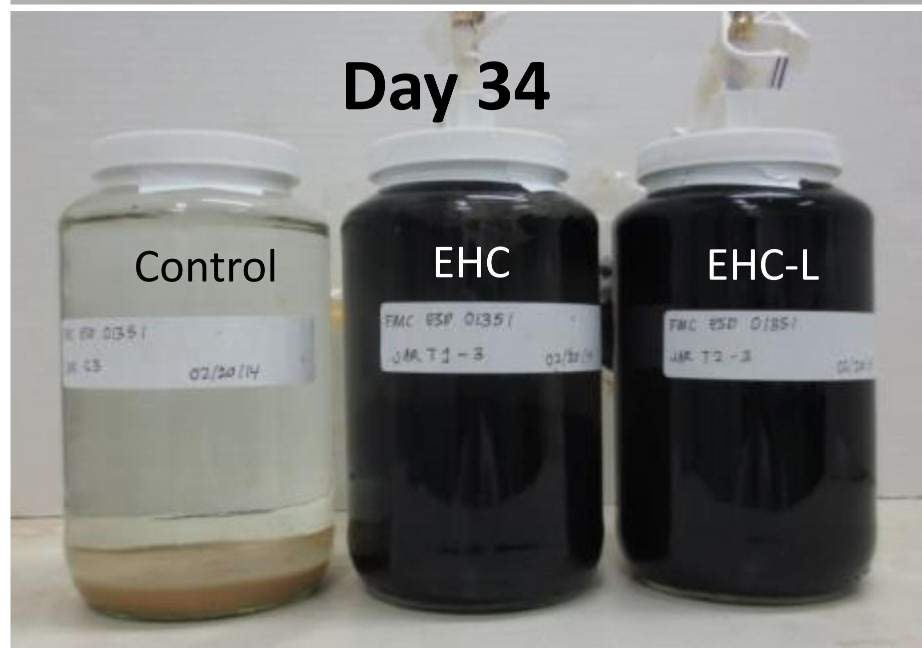
Sulfide Precipitation

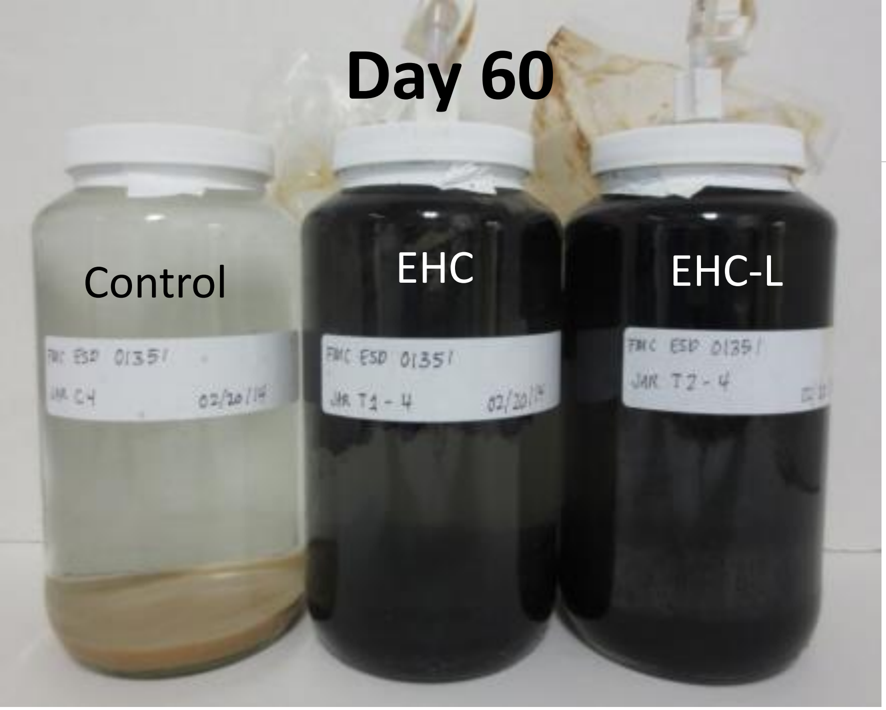


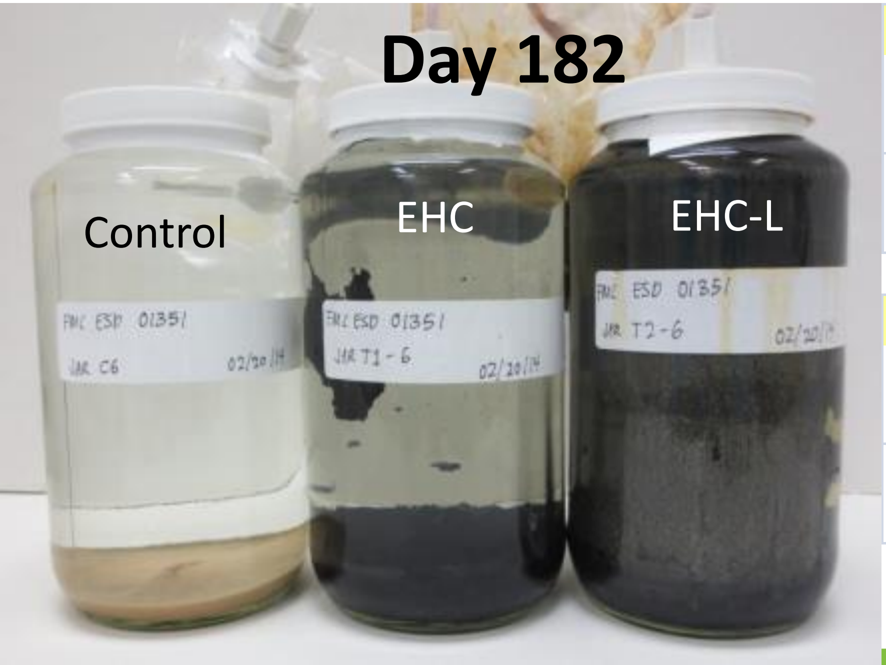
Precipitation of Sulfide











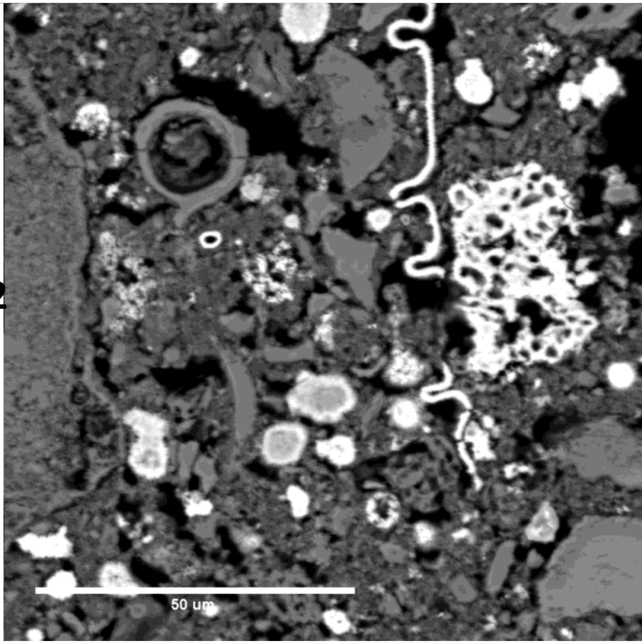
EHC Precipitate		
mg/Kg	Sulfide	31000
	Total Fe	210000
mMol/Kg	Sulfide	967
	Total Fe	3760

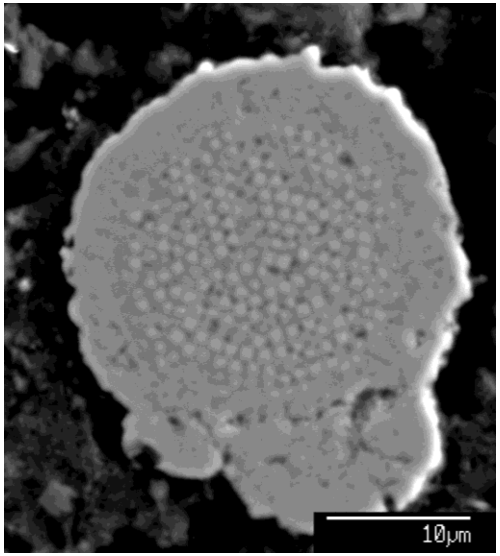
EHC-L + Iron Precipitate		
mg/Kg	Sulfide	42000
	Total Fe	130000
Mmol/Kg	Sulfide	1310
	Total Fe	2328

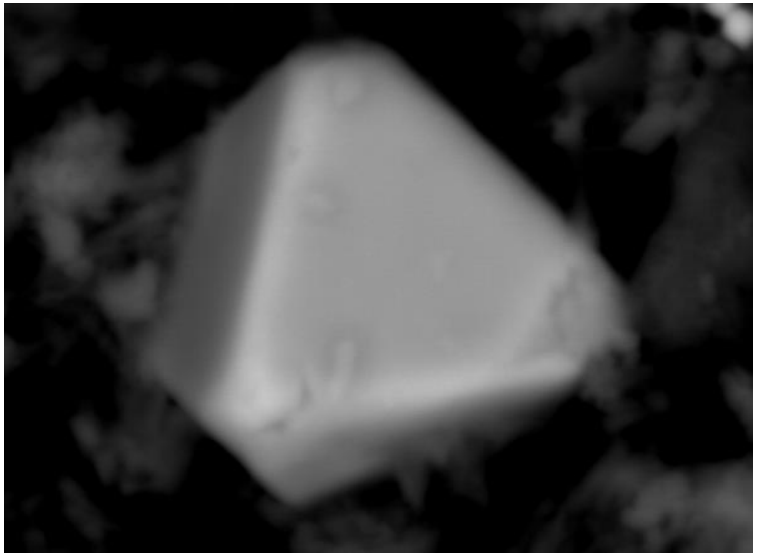
Process generates reactive FeS

3,000 mg/L sulfate + Fe^{2+}:

- Produces framboidal and euhedral pyrite
- Produces a 1 to 5 μM thick FeS coating 1.2 ft^2
- Large surface area increases rate of biogeochemical degradation







FeS Precipitation

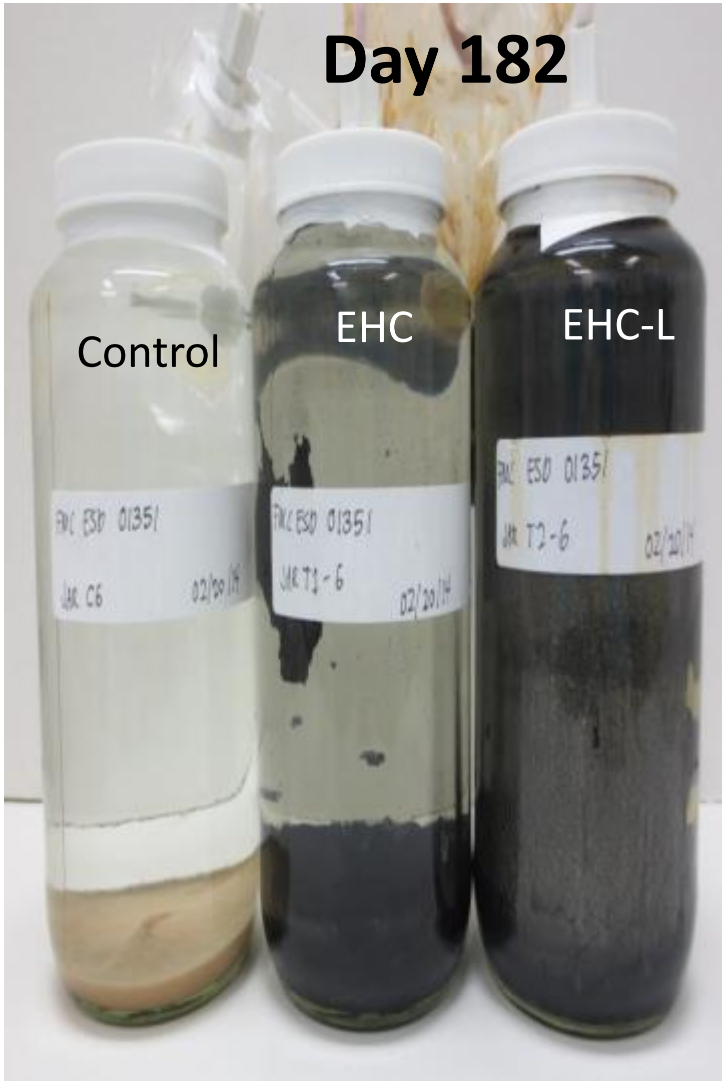
FeS does not fill pore space

Reduction of 1 Liter of 3,000 mg/L of sulfate and precipitation as ferrous sulfide produces:

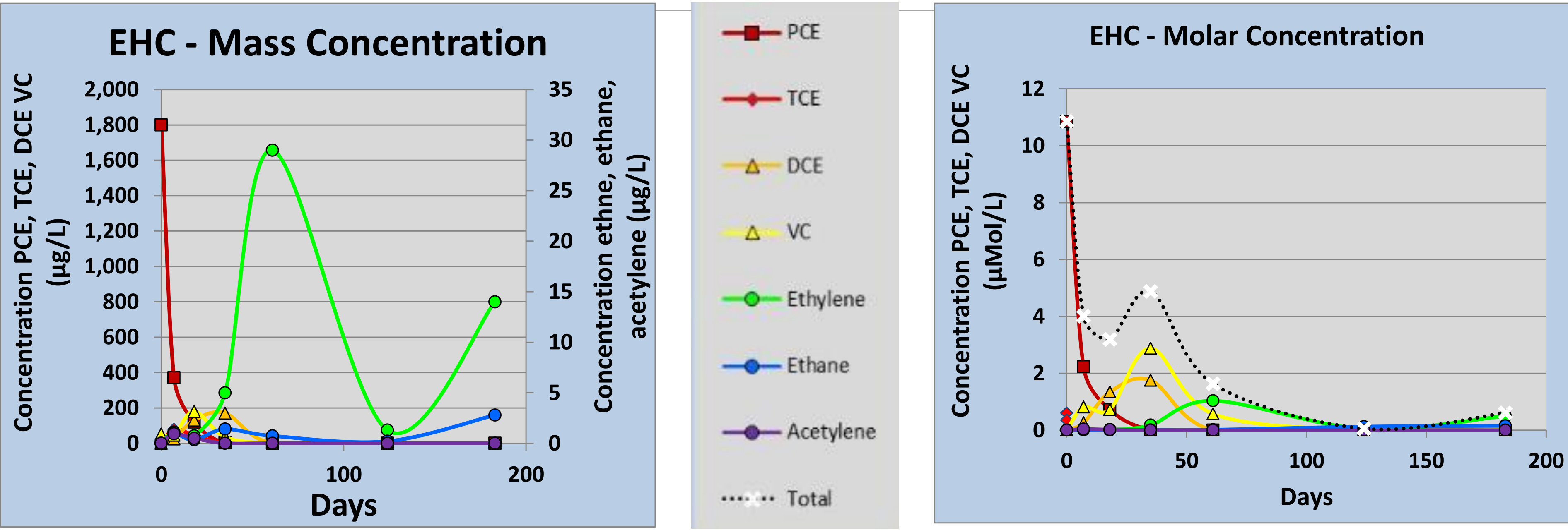
0.56 cm^3 Mackinawite (FeS, 4.9 g/cm^3)
~0.05% of volume

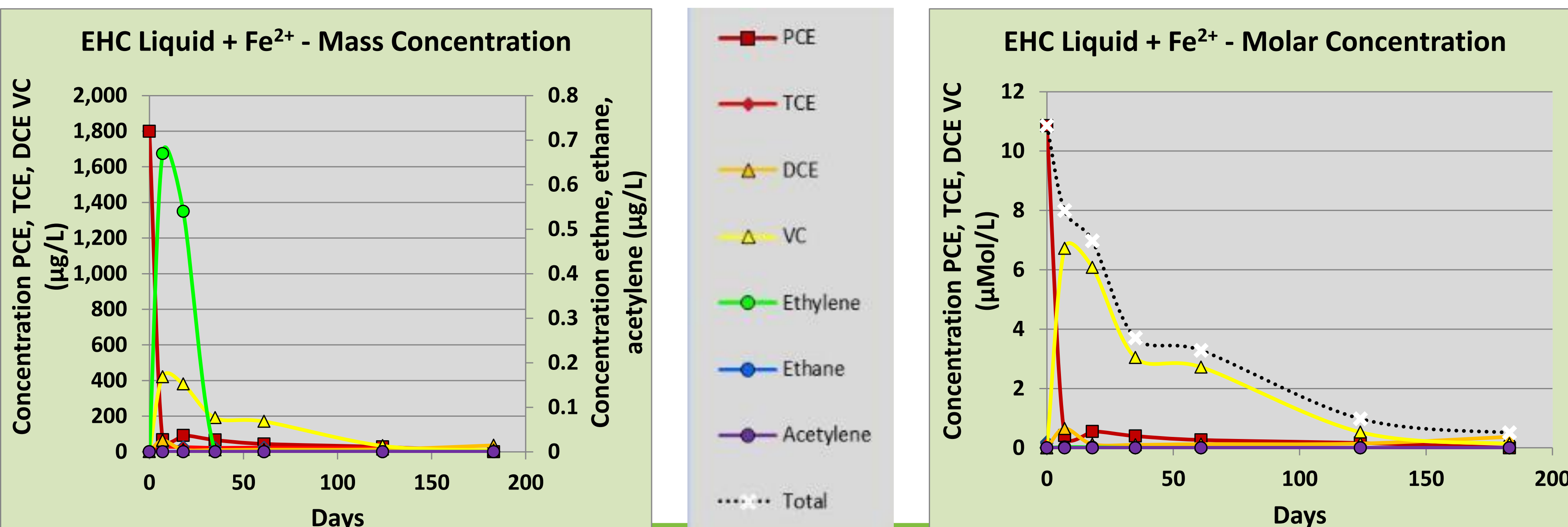
0.38 cm^3 Pyrite (FeS_2, 4.8 to 5.0 g/cm^3)
~ 0.04% of volume

Significant reductions in hydraulic conductivity would not be expected from FeS precipitation



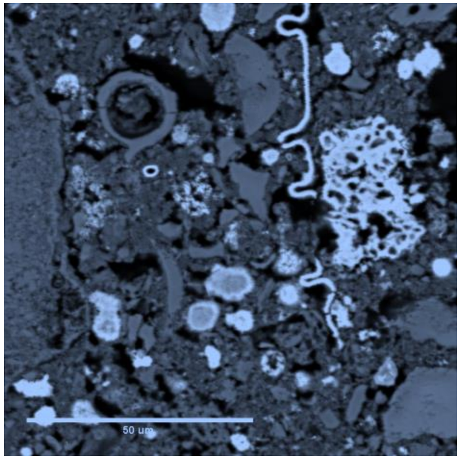
VOC Analytical Results



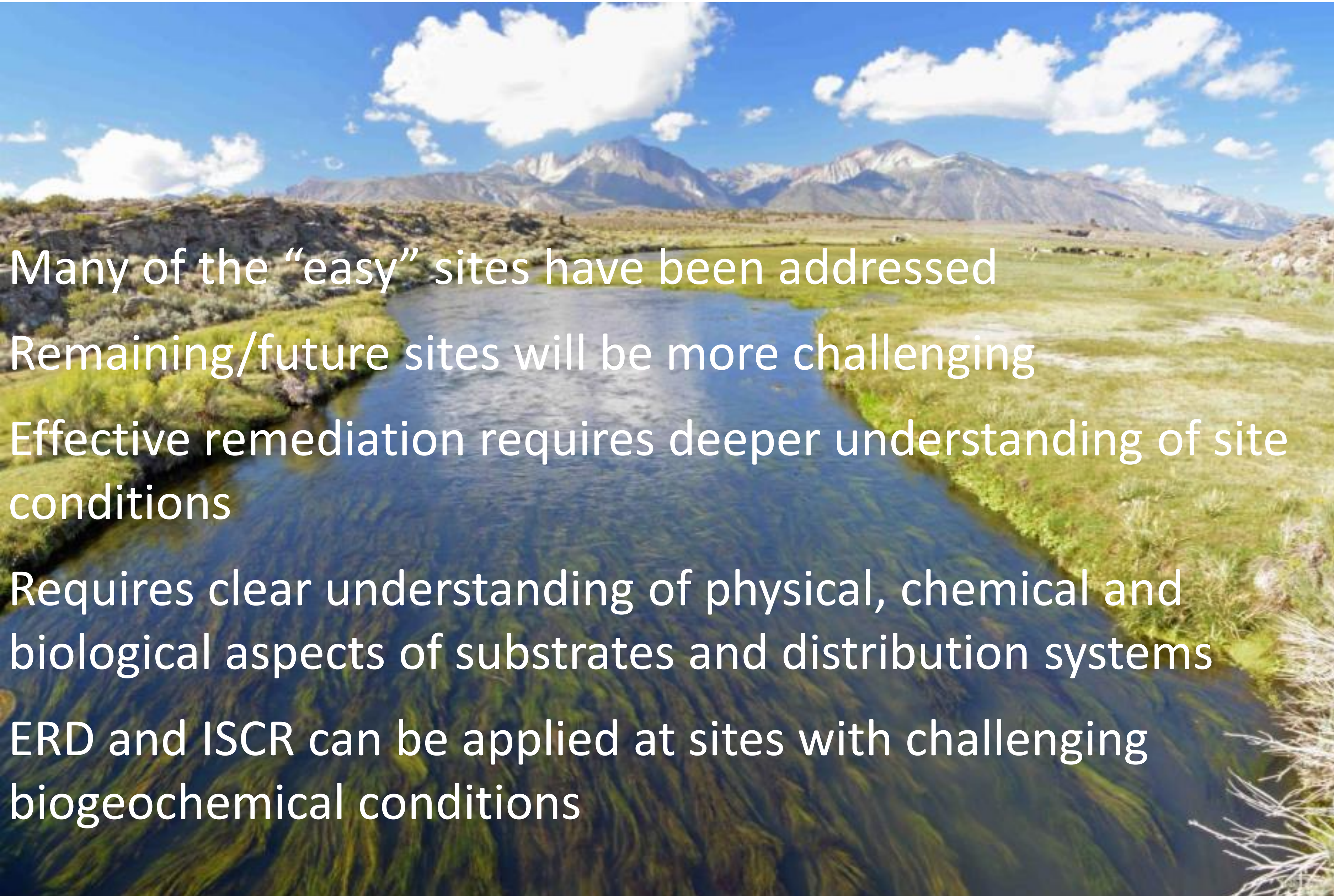


Bench Test Summary

- **Addition of EHC and EHC-Liquid will reduce sulfate to sulfide.**
- **Sulfide precipitates as ferrous sulfide**
- **Removal of sulfate and sulfide allows for complete reductive dechlorination of PCE**
- **Iron sulfide precipitation is insignificant relative to pore space occlusion**
- **However, large surface area of FeS precipitates**
- **FeS promotes biogeochemical degradation of chlorinated ethenes**



Conclusion



- Many of the "easy" sites have been addressed
- Remaining/future sites will be more challenging
- Effective remediation requires deeper understanding of site conditions
- Requires clear understanding of physical, chemical and biological aspects of substrates and distribution systems
- ERD and ISCR can be applied at sites with challenging biogeochemical conditions

Environmental Solutions

Thank You

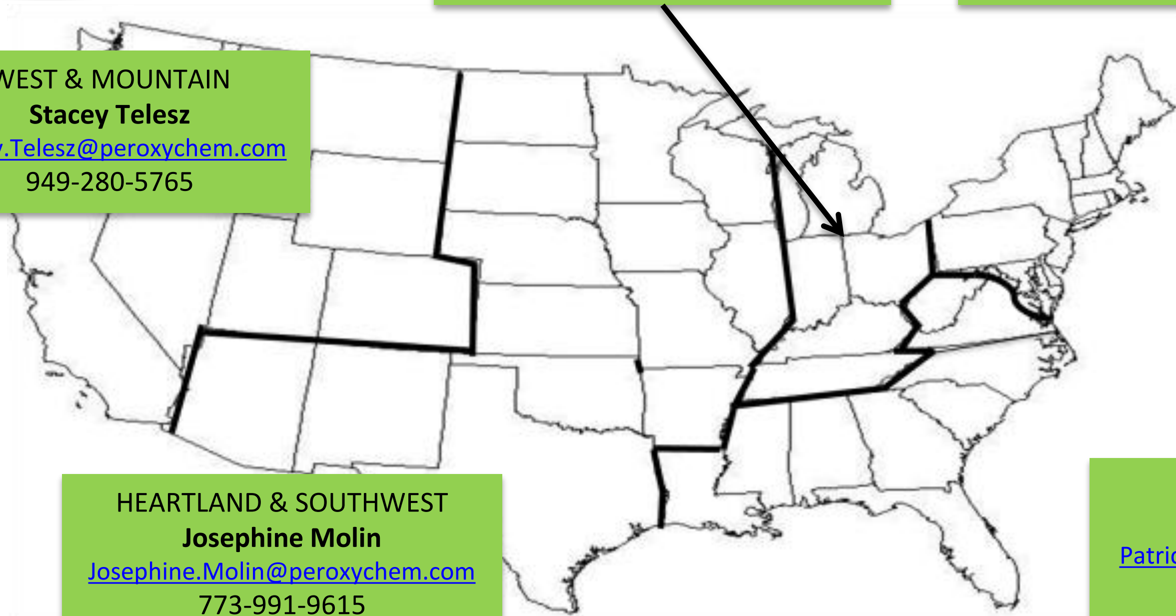
PeroxyChem

Environmental Solutions Team

MIDWEST
John Valkenburg
John.Valkenburg@peroxychem.com
517-669-5400

Mississauga Lab
Sandy Owen
sandra.owen@peroxychem.com
905-273-5374

WEST & MOUNTAIN
Stacey Telesz
Stacey.Telesz@peroxychem.com
949-280-5765



NORTHEAST,
INCLUDING DC METRO
Ravi Srirangam, Ph.D.
Ravi.Srirangam@peroxychem.com
312-480-5250

HEARTLAND & SOUTHWEST
Josephine Molin
Josephine.Molin@peroxychem.com
773-991-9615

SOUTHEAST
Pat Hicks, Ph.D.
Patrick.Hicks@peroxychem.com
919-280-7962

Technical Application Managers

Subject matter experts and market segment focused

Dan Leigh P.G., C.Hg.
DoD Programs
Daniel.Leigh@peroxychem.com
925-984-9121

Alan Seech, Ph.D.
R&D and Soil Treatment
Alan.Seech@peroxychem.com
949-388-7065

Fayaz Lakhwala, Ph.D.
Consultants
Fayaz.Lakhwala@peroxychem.com
908-688-8543

Brant Smith, Ph.D.
Chemical Oxidation
Brant.Smith@peroxychem.com
603-793-1291