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# Biogeochemical Treatment of cVOCs

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# Outline



- Reductive technologies
- Biogeochemical treatment
- GeoForm
- Bench studies
  - Low sulfate aquifers
  - High sulfate aquifers
- Conclusions

# Reductive Processes

- Donation of electrons to contaminants of concerns transforming contaminants into different compounds

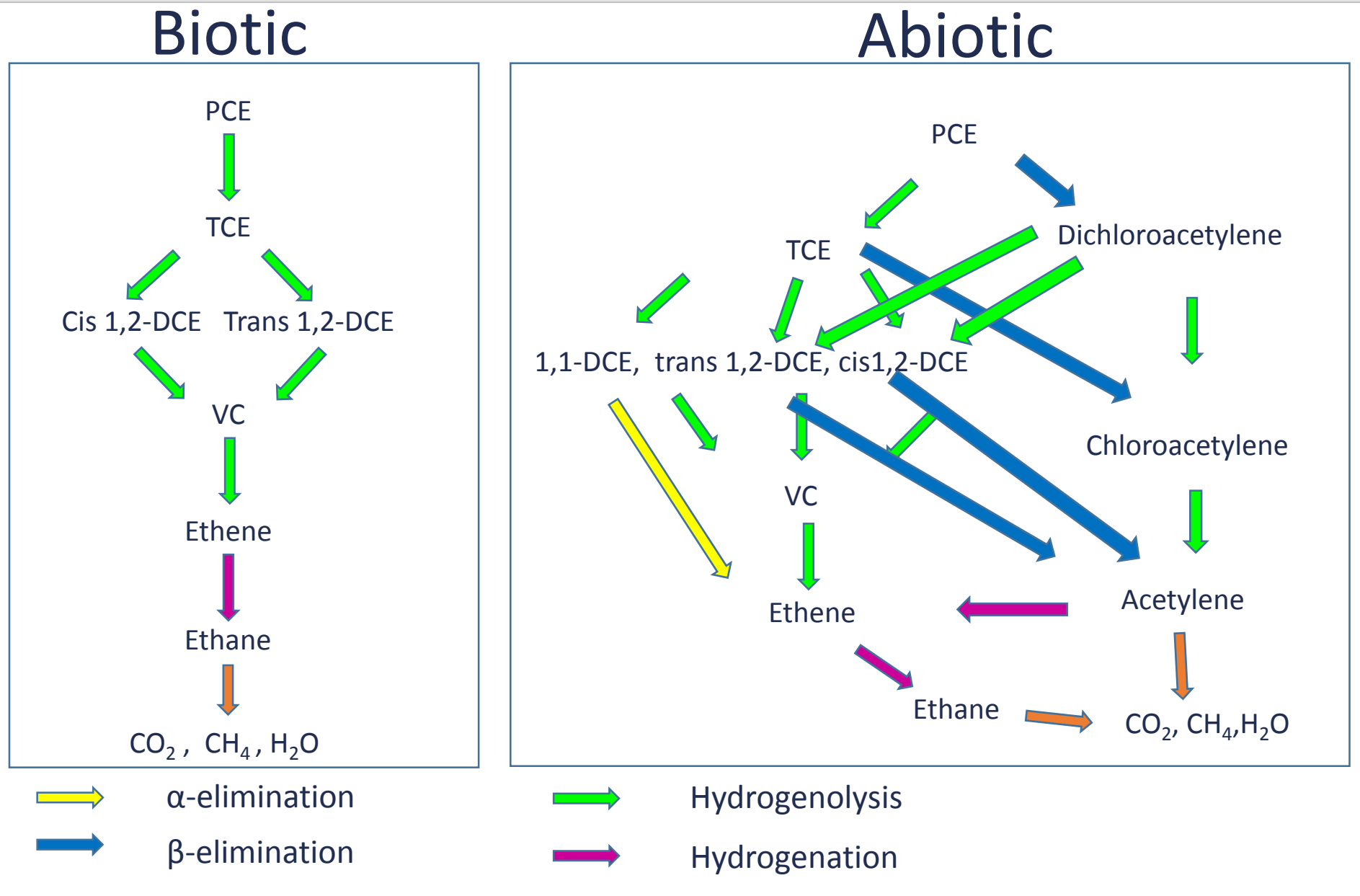
- Electrons tend to be preferentially transferred based upon thermodynamic properties

  Example: PCE>TCE>DCE>VC

- Targets oxidized contaminants:
  - cVOCs (PCE, TCE, TCA, etc)

Biotic vs Abiotic Processes

# Biotic and Abiotic Reductive Pathways



# Anticipated Change in CE Molar Concentration

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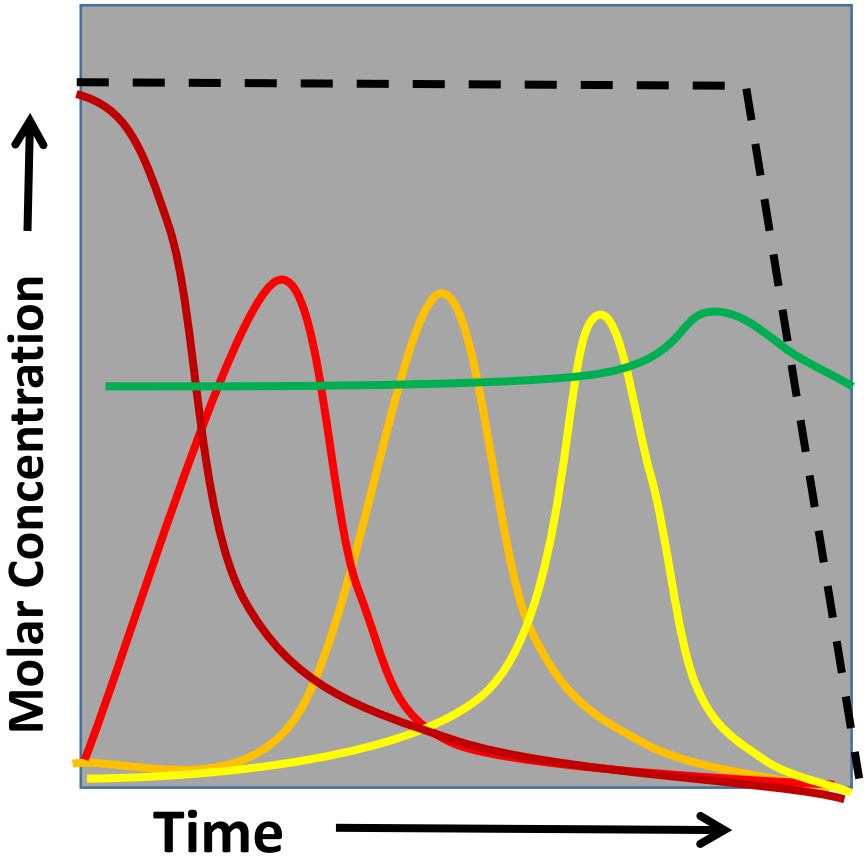
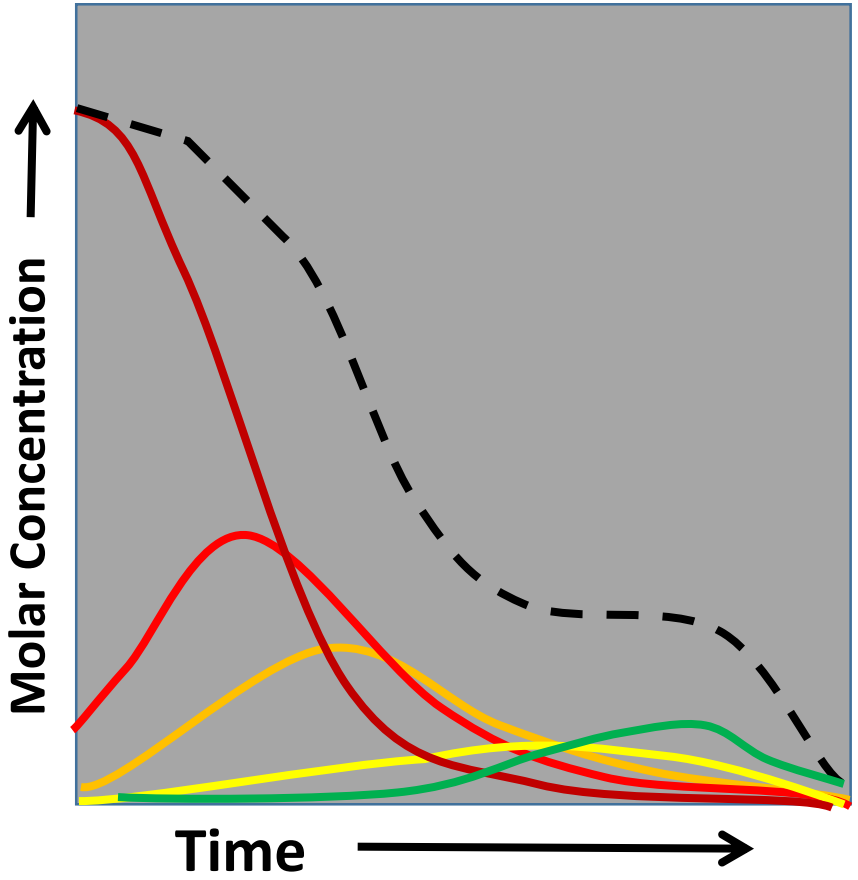
## Biological Degradation (Chlororespiration)




## Abiotic Degradation (β elimination)




PCE TCE DCE VC Ethene Total

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# Solid vs Liquid Amendments

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- Abiotic
  - Often solid state amendments
    - EHC, ZVI, etc
- Biotic
  - Typically liquid or emulsified amendments
    - ELS, lactate, oils, etc
  - Sometimes solid
    - EHC

- Liquid amendments
  - Injected
  - Distributed during injection
  - Some migration with groundwater
- Solid amendments
  - Typically physically emplaced or fractured
  - Little to no distribution or migration

# BioGeoChemical: Formation of Iron Sulfides

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**Injection of Reagents**

**Sulfate**
**+**
**Fe(II)**
**+**
**Electron donor**

## REACTIONS PROMOTED

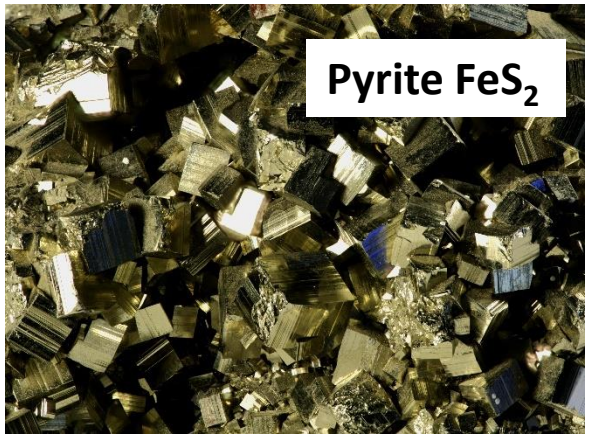
**Organic Substrate Fermentation**
**→ Reduced RedOx Conditions**

**Sulfate reduction by SRBs:**

$$2CH_2O_{(s)} + SO_4^{2-} + 2H^+_{(aq)} \rightarrow H_2S + 2CO_{2(aq)} + H_2O$$

**Precipitation of Ferrous Iron with Sulfide:**

$$Fe^{2+}_{(aq)} + H_2S_{(aq)} \rightarrow FeS_{(s)} + 2H^+_{(aq)}$$

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# Improved Distribution Properties

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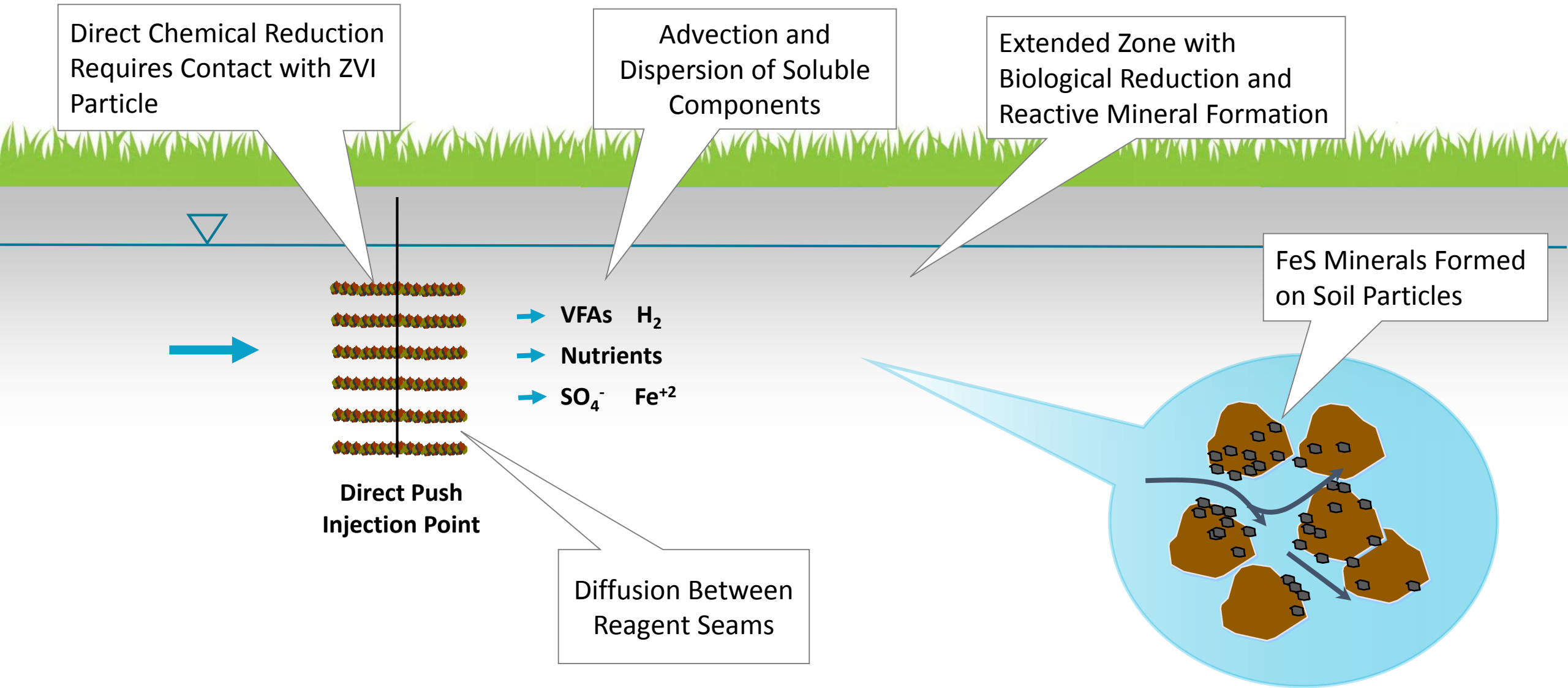
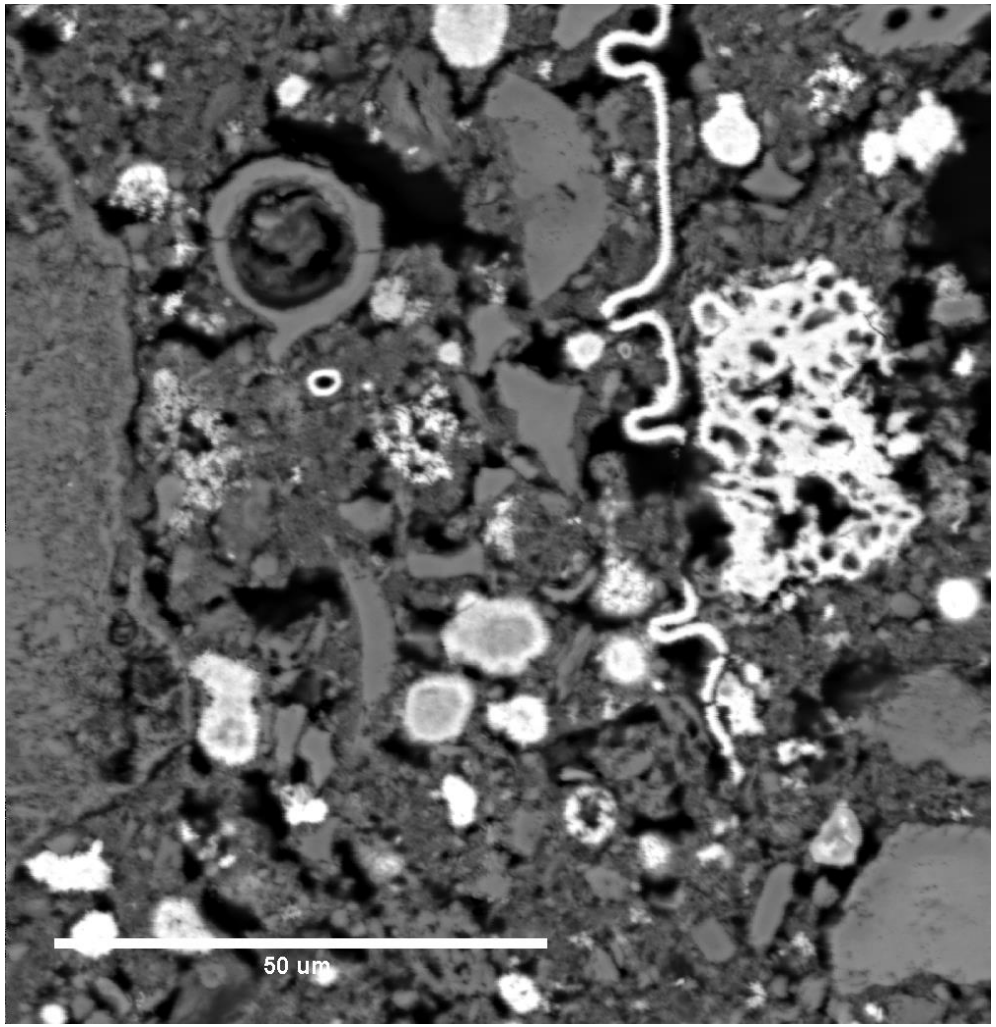
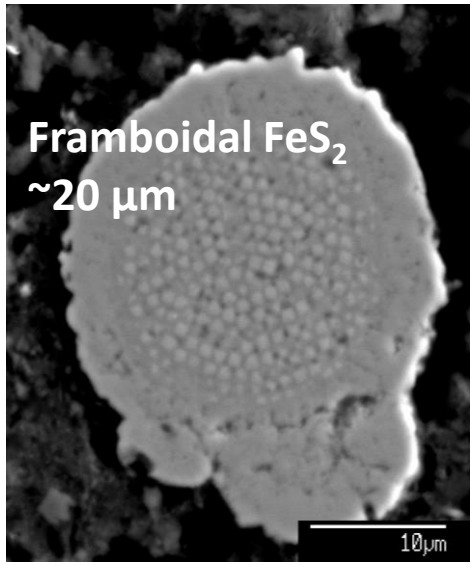
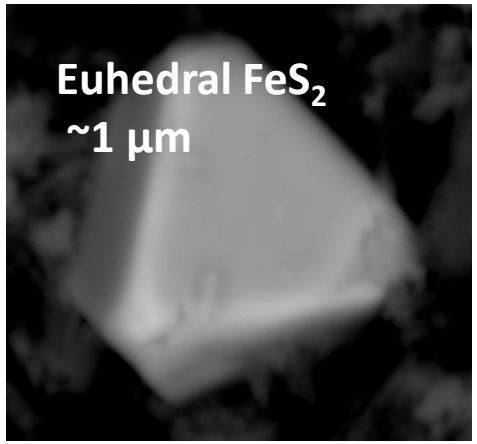


# Expanded Surface Area for Abiotic Pathway




Electron microprobe analyses performed on iron sulfide precipitation products estimated that 4.7 $ft^2$ of very reactive surface area was generated per liter of groundwater with 3,000 mg/L sulfate reduced to an estimated 3 µm thick FeS precipitate (Leigh et al).

| | Particle Size (µm) | Surface Area ($m^2$/kg) |
|---|---|---|
| Micro-Scale ZVI | 50-250 | ~5-30 |
| Framboidal Pyrite | 20 | ~10 |
| FeS Coatings | 3 | ~80 |
| Euhedral Pyrite | 1 | >200 |

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# BioGeoChemical

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## Benefits

- Soluble amendments will distribute in aquifer
- Biologically reduced sulfur and iron form solid-state iron sulfides
- High surface area
- Abiotic reductive pathway

## Challenges

- Selecting the appropriate ratios of Fe/S, pH buffer, and electron donor
- The limited solubility of Fe (II) at near neutral pH can make injection and distribution a challenge
- Most other soluble ISCR reagents available include a lower amount Fe(II)

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# GeoForm™

BIOGEOCHEMICAL REAGENT

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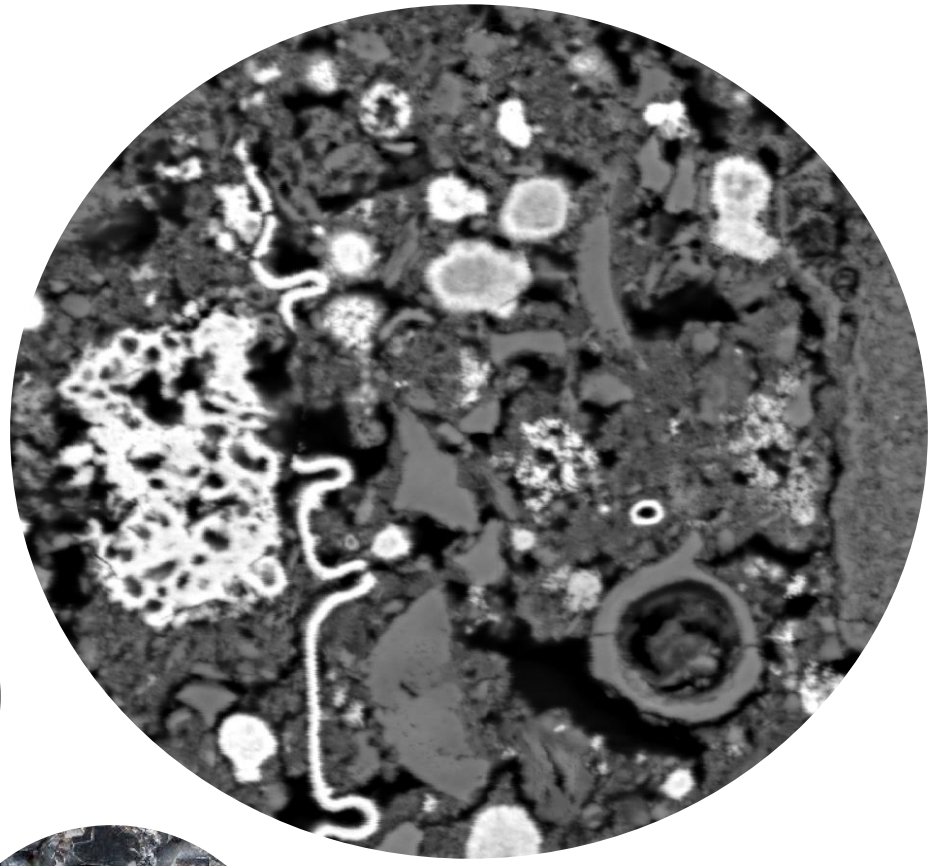
- All-In-One BioGeoChemical Reagent
- Provides All Building Blocks Needed for Reactive Mineral Formation
- Combines Sulfate, Ferrous Iron, Electron Donors, pH Buffer, and Nutrients
- Effective for Chlorinated Organics and Heavy Metals



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# GeoForm™ BIOGEOCHEMICAL REAGENT SOLUBLE

## GeoForm™ Soluble

Injects as a solution forming long lasting solids

Soluble Organic Carbon, Sulfate, Ferrous Iron, pH buffer and nutrients

Longevity of 2-3 years or more

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# GeoForm™ Extended Release

GeoForm™

BIOGEOCHEMICAL REAGENT EXTENDED RELEASE

Provides a longer lasting source of electron donor for continued rejuvenation of reactive mineral zone

Extended Release Organic Carbon, Micro-Scale ZVI, Sulfate, Ferrous Iron, pH buffers and nutrients

Longevity of 5-10 years or more

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# Enhanced Treatment

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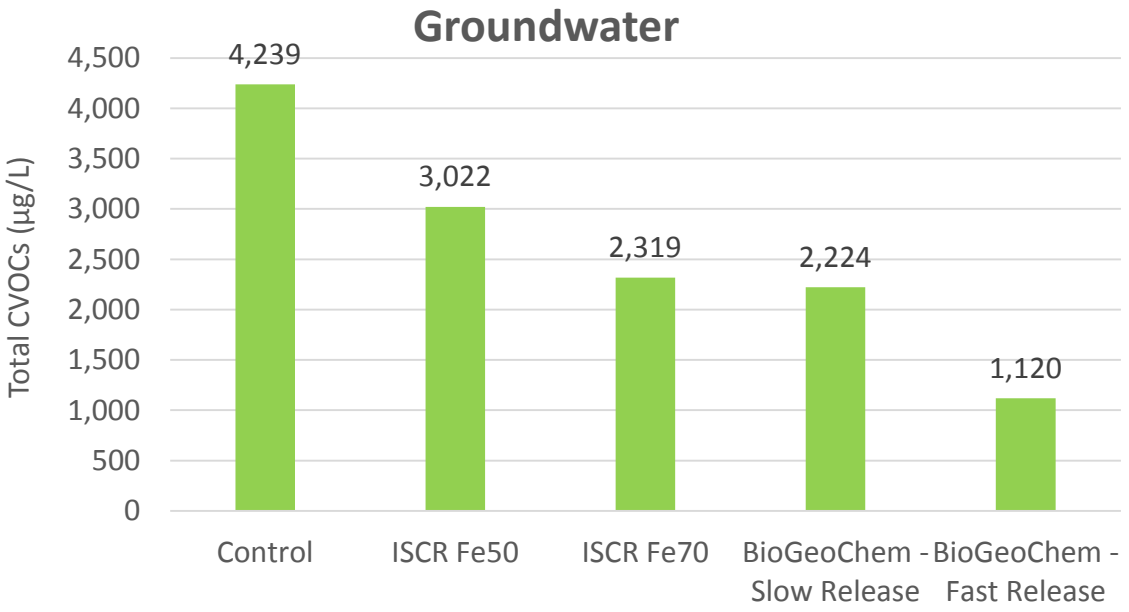
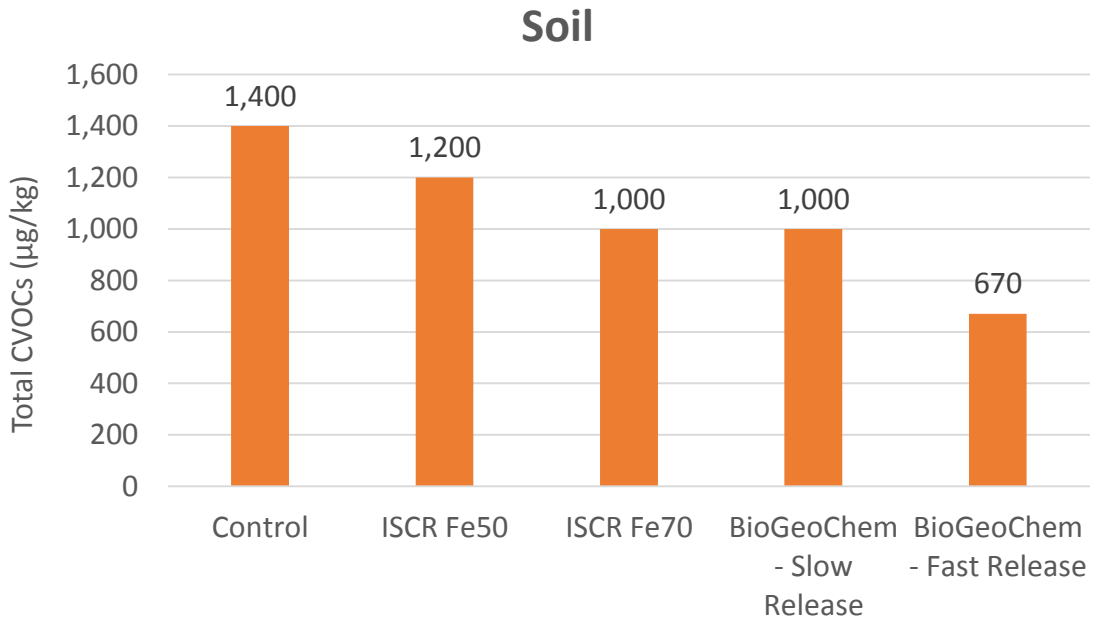
Biogeochemical has repeatedly shown to promote higher degradation rates relative to traditional ISCR or organic carbon substrate alone

>40% higher removal rates in comparative studies

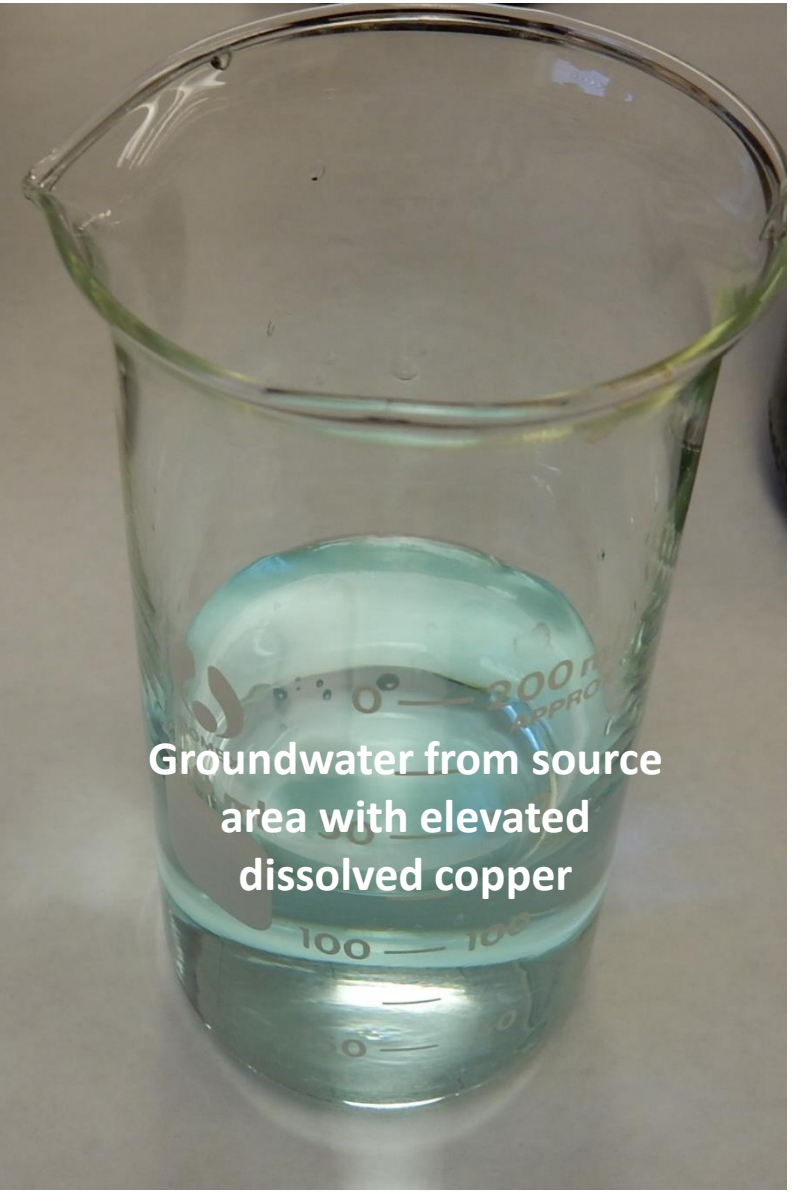
# Site 1: cVOC Bench Study

- Site with low pH conditions with no sign of biological degradation
- **62 to 156% higher removal rates** with GeoForm/Biogeochemical relative to traditional ISCR after 96 days
- Minimal generation of daughter products in all systems (<15 µg/L)
- Chromium non-detect in all amended systems



# Site 2: CVOCs and Heavy Metals




- Site with low pH conditions and little evidence of biological degradation
- Baseline site conditions:
  - PCE ~2,500 µg/L; Heavy metals ~1,700 µg/L (primarily Cu, Ba, Cd, Zn)
  - pH = 4.3; ORP = 300 mV; Sulfate = 46 mg/L
- **42 to 66% higher removal rates** with GeoForm relative to ERD after 56 days

| Reagent | Reagent Dose in GW (g/L) | % Reduction in Total CVOCs | % Reduction in Heavy Metals |
|---|---|---|---|
| ELS® Microemulsion | 1 | 58 | 90 |
| | 3 | 69 | 70 |
| GeoForm™ Extended Release | 2 | 96 | 94 |
| | 4 | 98 | 91 |

# Site 3: ISCR in High Sulfate Aquifer

**Site Conditions:**

- Elevated PCE >2,000 µg/L
- Sulfate up to 3,000 mg/L
- Aerobic Aquifer (DO ~5.0 mg/L)
- Previous bio only pilot tests unsuccessful - Potential sulfide inhibition

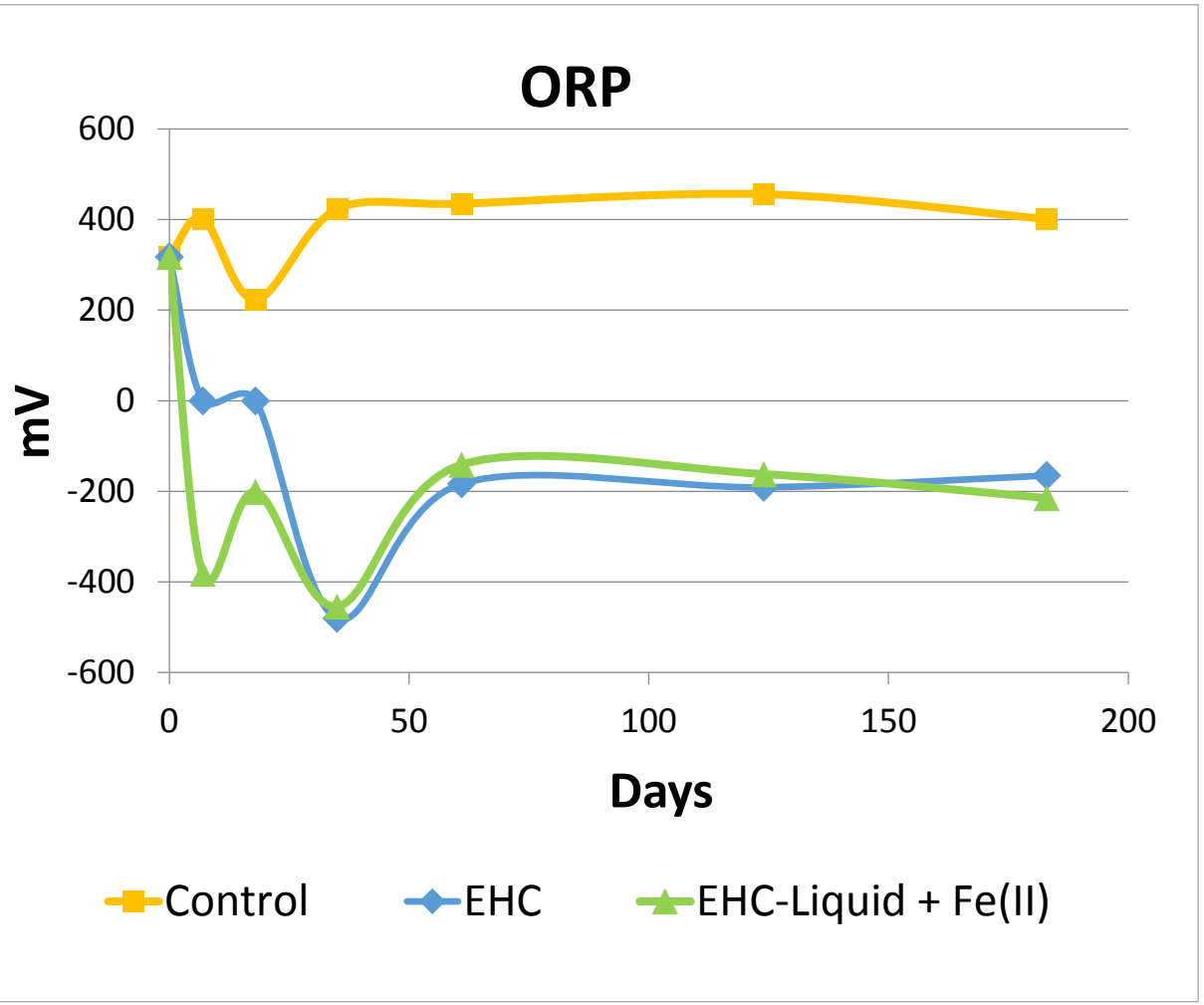
**Bench Set-Up:**

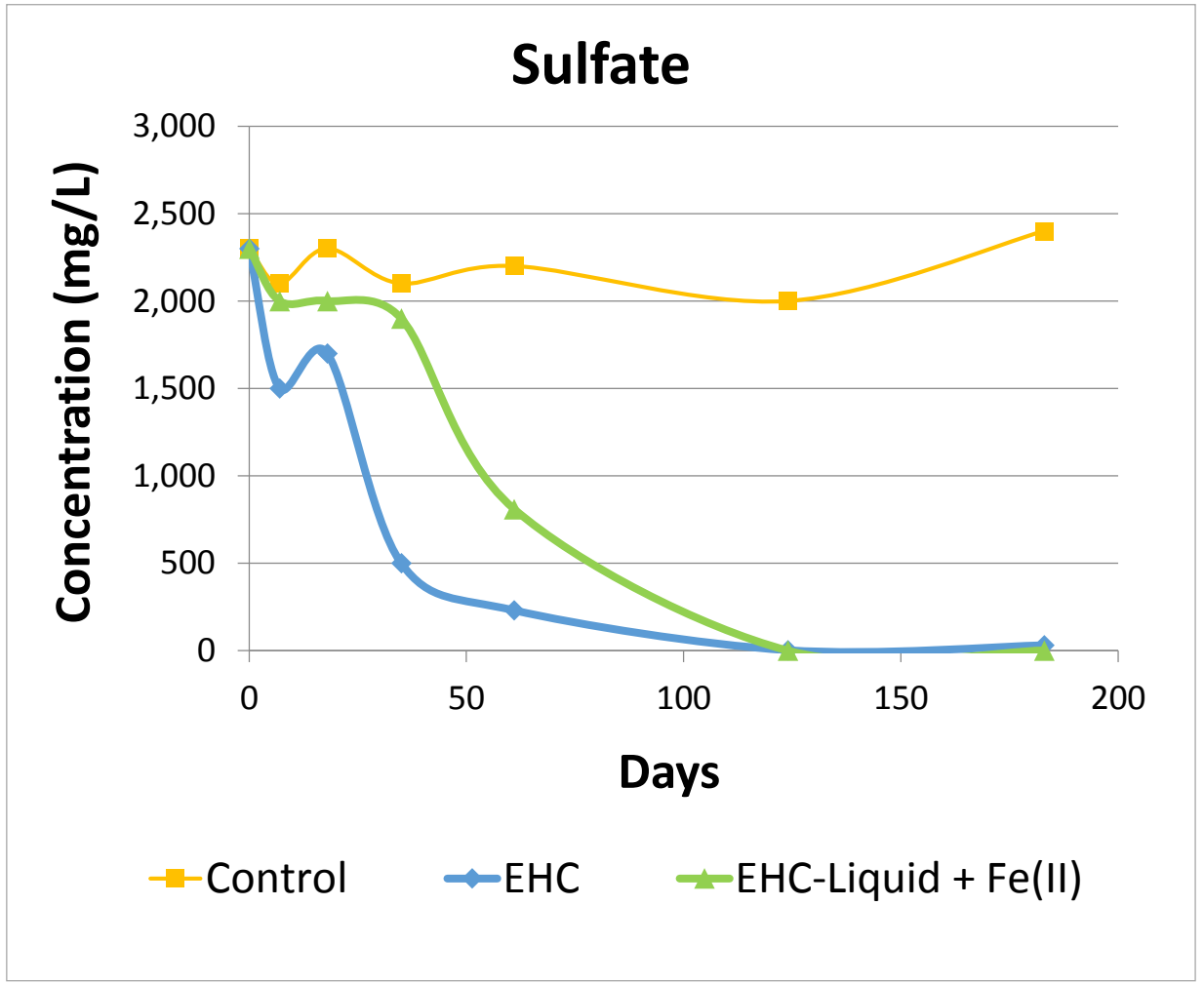
Microcosms set up with GW and sediment from the site:

- Control
- EHC: 10 g/L (60% organic carbon + 40% ZVI)
- EHC Liquid: 10 g/L ELS + 14 g/L ferrous gluconate

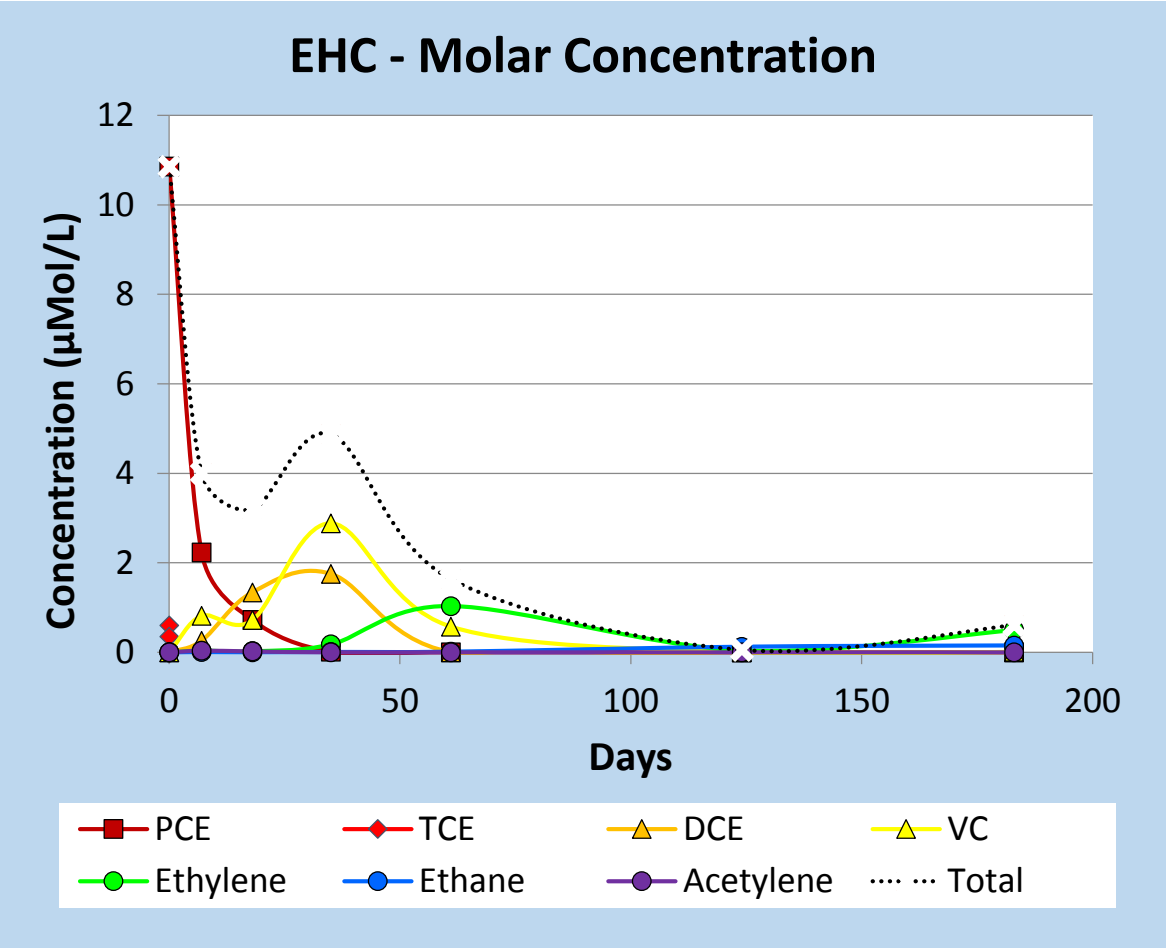
Treatment systems inoculated with DHC ~ $1X10^8$ Cells/L

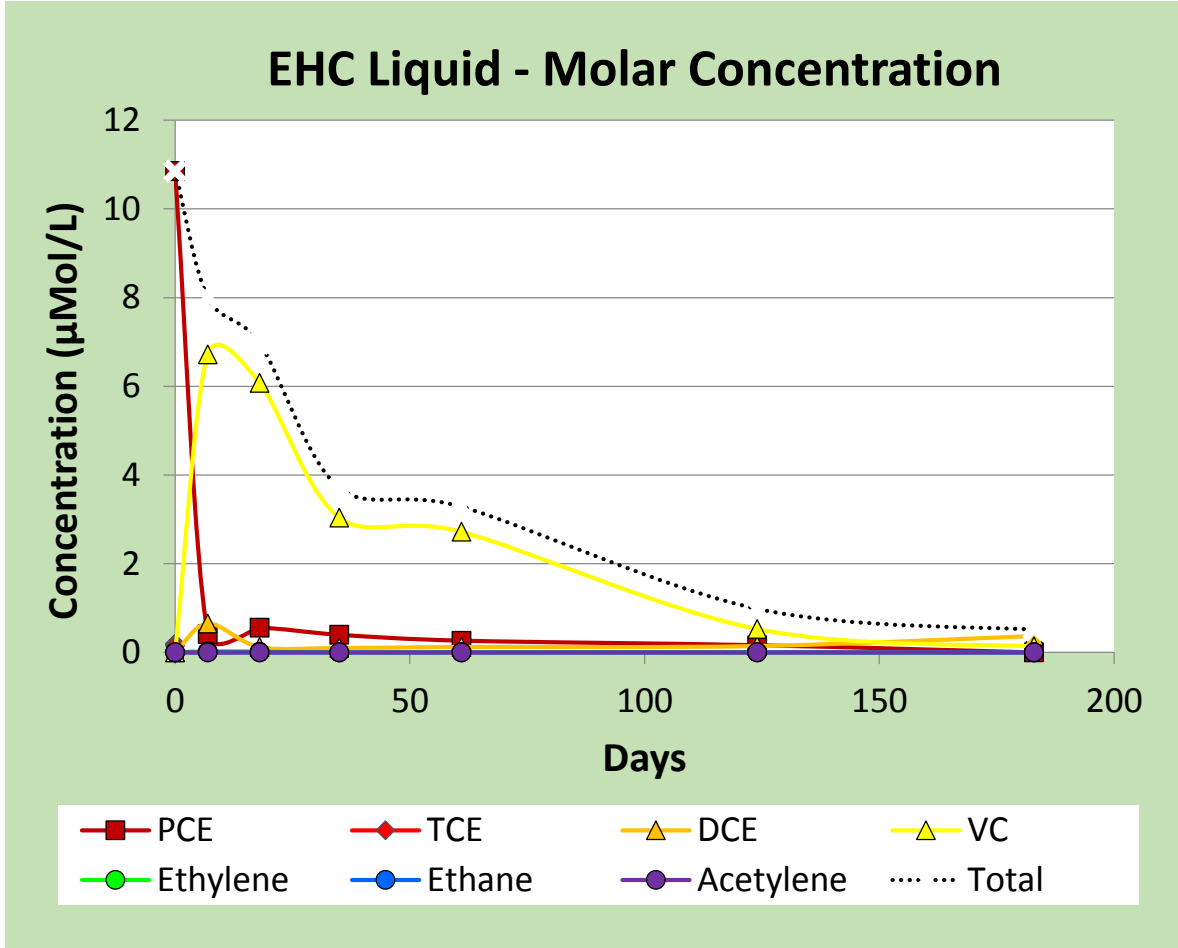
# Sulfate Reduction



# VOC Analytical Results




Less than Stoichiometric conversion to daughter products → Abiotic degradation pathway promoted in both systems

# Summary



- Biogeochemical
  - Soluble reagents distribute into the aquifer
  - Form iron sulfides
  - High surface area allows for great contact and treatment of cVOCs
- Geoform
  - Soluble-quick release
  - Solid-extended release
- High sulfate aquifers
  - Promote biogeochemical by adding iron and organic

# Questions

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